The Development Of Group II Metals (Ca/Mg) As Promoter Or Bimetallic Couple For Ni/ɣ-Al_2O_3 Catalyst For Application Of Aqueous Phase Reforming Of Glycerol

by

Nadzirah Binti Azmi
16884

Dissertation submitted in partial fulfilment of
the requirement for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

MAY 2015

Universiti Teknologi PETRONAS
32610 Bandar Seri Iskandar
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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Approved by,

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(Dr. Mohammad Tazli Bin Azizan)

UNIVERSITI TEKNOLOGI PETRONAS
SERI ISKANDAR, PERAK
May 2015

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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NADZIRAH BINTI AZMI

ABSTRACT

With development of technology now day, the valorisation of glycerol is one of the solutions to solve problem of excess amount of glycerol produced in biodiesel industry. In order to contribute to the development of glycerol research, aqueous phase reforming (APR) is used to valorise the glycerol. The main objectives of this project is to study the potential value added chemicals can be produce from aqueous phase reforming of glycerol using Ni/ɣ-Al_2O_3 catalyst promoted or bimetallic couple with Group II metals (Ca/Mg). For this study, thirteen catalysts will be synthesised using incipient wetness impregnation method (IWI). 10wt% of nickel loading was deposited on gamma alumina support. The effect of different metal loading of calcium and magnesium (0.5%, 3.0%, 5.0% and 7.0%) on the physiochemical properties of catalyst has been investigated. Then the synthesised catalysts will undergo several characterization techniques such XRD, BET analysis, SEM, FESEM and TPR to distinguish its characteristics. Result from XRD shows that the addition of calcium and magnesium increased the intensity of the catalyst. From BET analysis, it was found that the addition of metals like nickel, calcium and magnesium decreased the surface area, pore volume and size. From the images that have been captured from SEM and FESEM, the particles were visible well dispersed on the support. For TPR, the reduction temperature of 10% Ni is 660°C. The catalytic activity gamma alumina supported nickel; calcium and magnesium were evaluated in an autoclave reactor at 230°C, 10 bar 450 rpm. The results obtained from the reactor were good enough. The addition of 3% alkaline metals into the support seems to be optimum amount of metals in order to have good APR reaction. The value added chemicals that have been produced that useful to industry are 1, 3-propanediol, propionaldehyde, propylene glycol, propanol, ethanol and ethylene glycol.

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LIST OF ABBREVIATION AND NOMENCLATURES

APR	Aqueous Phase Reforming
Ni	Nickel
ɣ-Al_2O_3	Gamma Alumina
Ca	Calcium
Mg	Magnesium
BET	Brunauer, Emmett and Teller method
SEM	Scanning Electron Microscopy
XRD	X-Ray Diffraction
FESEM	Field Emission Scanning Electron Microscopy
TPR	Temperature Programmed Reduction
HPLC	High Performance Liquid Chromatography

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CHAPTER 1

INTRODUCTION

1.1 Background

Nowadays people began to realize the importance of green technology toward sustainability development. What is meant by sustainability development is the development that fulfils the needs of the existing without affecting the needs for future generations. By utilizing green technology which is environmental friendly, it can help protect the nature from global warming or any negative impacts.

One of the demand products based on green technology is biodiesel. From Monthly Biodiesel Production Report of U.S. Energy Information Administration, it stated that in July 2014, the production of biodiesel was 121 million gallons and 11 million gallons higher than production in June 2014 [1]. The potential of biodiesel in term of economy and environment make it industry increasing from time to time.

But the problem is biodiesel production will produce crude glycerol as a main by-product. It will generate 10 % (w/w) glycerol every process which mean if 100 million gallons biodiesel produced, 10 million gallons of glycerol [2]. This problem has made people take initiative to exploit the glycerol from waste product to value added product.

1.2 Problem Statement

The rapid growth of biodiesel production had led to excess amount of crude glycerol. This situation had led to falling of glycerol price in market. Besides, the cost of production biodiesel is higher compared to diesel. It is reported that most of the total production came from the cost of raw material such as vegetable oils and animal fats. By valorising the crude glycerol to value added chemicals, it can cover back the total production cost of biodiesel and the same time improves the glycerol market. Based on the literature, Aqueous Phase Reforming (APR) reaction is one of effective way to valorise glycerol, become value added chemicals.

1.3 Objectives

1. To synthesize and characterize Ni/ɣ-Al_2O_3 catalyst and Ni/ ɣ-Al_2O_3 promoted or bimetallic couple with Group II metals (Ca/Mg).
2. To study the potential value added chemicals can be produce from Aqueous Phase Reforming of glycerol using Ni/ɣ-Al_2O_3 catalyst and Ni/ ɣ-Al_2O_3 promoted or bimetallic couple with Group II metals (Ca/Mg).

1.4 Scope of Study

The scopes of study of this project are:

1. Setting up a laboratory scale experiment to prepare Ni/ɣ-Al_2O_3 catalyst using incipient wetness impregnation method.
2. Studying the effect of promoting the catalyst with Ca/Mg.
3. Characterization of catalysts using XRD, BET analysis, SEM, FESEM and TPR.
4. Pure glycerol will be used to represent crude glycerol which is main by-product of biodiesel production.
5. Evaluating the performance of catalysts.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Depletion of non renewable resources such as petroleum which is limited resources that cannot be replaced has lead to the expansion usage of renewable resources like biomass as a fuel. In addition, the usage of renewable resources can reduce carbon dioxide and other global warming emissions [3].

Biomass is organic matter that can be converted into liquid fuels which is biofuels. One of the common biofuels is biodiesel. The raw materials to produce biodiesel are vegetables oils, fats and greases and the credibility of biodiesel as transportation fuel also had been commercially proven [4].

Today, demand of biodiesel is increasing rapidly. Based on Figure 2.1, it illustrated that the growth rate for biodiesel is forecast up to 10 % by 2020. This matter shows a good indication to biodiesel industry in term of profitability that the investors will gain when involved in this industry. But the problem is when the production of biodiesel increases, the by-product which is glycerol also increases.

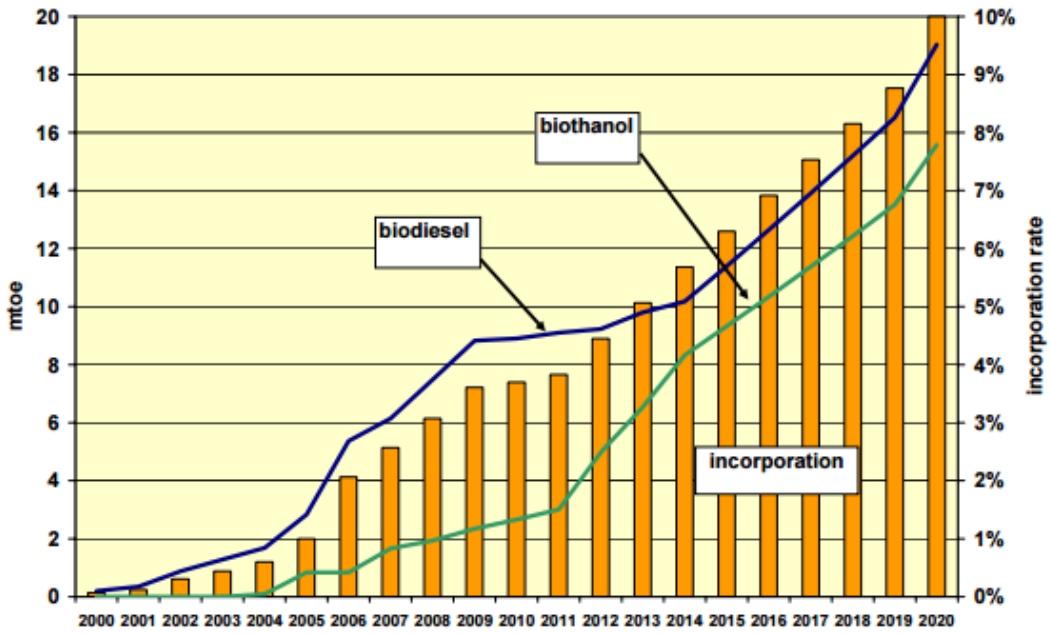


FIGURE 2.1 Demand of Biodiesel and Bioethanol until 2020 in Europe [5]

But still, glycerol is a useful by-product. The valorisation of glycerol to high value chemicals is an approach to overcome the problem of surplus amount of glycerol in the market. Many researched had been done to utilized glycerol such as pyrolysis, steam reforming, partial oxidation, autothermal reforming and aqueous phase reforming [6]. With the help of advance technology, redundant supply of glycerol can be solved and consequently it can increase the economic potential of biodiesel industry.

2.2 Glycerol

Glycerol is a trihydroxyl sugar alcohol compound. The other names of glycerol are glycerine, 1, 2, 3-propanetriol, glycerine, glyceritol, glycyl alcohol and trihydroxypropane. It is clear, colourless, syrup liquid or solid (below 17.9 °C). Glycerol taste sweet and non-toxic [7] .

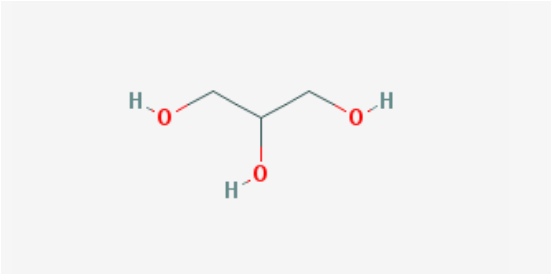


FIGURE 2.2 Chemical Structure of Glycerol [7]

Glycerol can be obtained either from synthetic or natural route. For synthetic method, the raw material is propylene and undergoes epichlorohydrin process. In this process, propylene reacted together with chlorine to produce epichlorohydrin. Then epichlorohydrin will be hydrolyzed to form glycerol. But this method was not applied anymore because it is not economical [8].

Besides, glycerol can be produced as by-product from oils and fats processing such as soap production and fat splitting. The hydrolysis or transesterification of triglycerides which is found in fats and oils will produce glycerol. In the midst of modern technology, most of production of glycerol came from biodiesel industry [8].

2.2.1 Usages of Glycerol

Additionally, glycerol can be used as raw material in health care (cough syrups), personal care (skin care products), food and beverages (sweeter), polyether polyols and alkyd resins cellophane (surface coating) [9]. Figure 2.3 shows a pie chart of current glycerol usage.

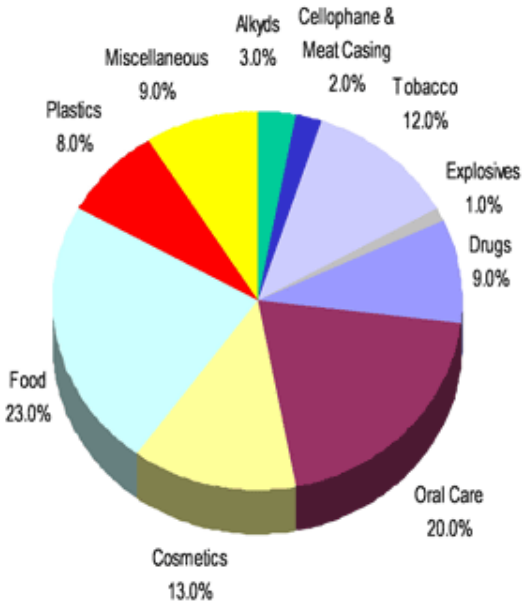


FIGURE 2.3 Glycerol Usage [10]

2.2.2 Market of Glycerol

Referring to market report published by Transparency Market Research, "Glycerol Market by Source (Biodiesel, Fatty Acids & Fatty Alcohol), by Applications (Personal Care, Alkyd Resins, Polyether Polyols, Others), Downstream Opportunities (Propylene Glycol, Epichlorohydrin, 1, 3 Propanediol and Others) – Global Industry Analysis, Size, Share, Trends, Growth and Forecast, 2012 - 2018," the global demand for glycerol was 1, 995.5 kilo tons in 2011 and is expected to reach 3, 060.4 kilo tons by 2018. While for revenues, glycerol demand is expected to reach $2.1 billion by 2018 [11].

This report shows that glycerol is a potential product that can give profit to those dealing with it. In addition, glycerol which is an environmental friendly chemical is one of the promising opportunities to be commercialized also in future.

2.3 Valorisation of Glycerol to Value Added Chemicals

Glycerol is a versatile chemical compound. It can be reformed to other useful chemicals with different approaches such as pyrolysis, steam reforming, partial oxidation, autothermal reforming and aqueous phase reforming. Pyrolysis is a thermal breaking method that operated in the absence of oxygen. The process must consider the heat input and it is extremely endothermic reaction. There are two major parts in a pyrolysis environment which are dehydration and dehydrogenation. Dehydration generates hydroxyacetone and 3-hydroxypropanal while dehydrogenation produces glyceraldehydes and dihydroxyacetone. Steam reforming is combination of pyrolysis with water gas shift reaction. This process occurs under ambient pressures in gaseous phase and required heat to vaporize the reactants. Partial oxidation is a process that converts glycerol with substoichiometric numbers of oxygen. High temperature and fast oxygen consumption rate require due to exothermic reaction of oxidation. Autothermal reforming is division of partial oxidation process. But the different is glycerol is fed simultaneously with water under partial oxidation conditions. In order to maintain self sustaining operation, the heat of reaction should be higher than zero [6].

TABLE 2.1 Products of Valorisation of Glycerol

Techniques	Products
Pyrolysis [12]	**Gas** Hydrogen, Carbon monoxide, Carbon dioxide, Methane and Ethylene. **Liquid** Acrolein, acetaldehyde, acetone, methanol, ethanol, water and char.
Steam reforming[13]	**Gas** Hydrogen, Carbon monoxide, Carbon dioxide and Methane. **Liquid** 2-propenal, 2-methyl-2cyclopentenona, phenol (Catalyst

	used : Pt/ɣ-Al_2O_3) 1,2-propanediol, 1-hydroxy-2-propanone, acetic acid and 2-propenal (Catalyst used : Pt/ZrO_2 and Pt/Ce4Zr1a)
Partial oxidation and Autothermal reforming [14]	**Gas** Hydrogen, Carbon monoxide and Carbon dioxide **Liquid** Acrolein and hydroxyacetone

The literature review about aqueous phase reforming will be further discussed in section 2.3.1.

2.3.1 Aqueous Phase Reforming

Aqueous phase reforming (APR) is reforming reaction done in liquid phase. This reaction occurs in low temperature around 127 °C to 227 °C and medium pressure about 10 bar to 60 bar which are the favourable conditions for water-gas shift reaction and the possibility to generate hydrogen with low amounts of carbon monoxide in a single reactor is high. By operated in low temperatures, it can minimize unwanted decomposition reactions. APR is also an energy saving reaction because it produces hydrogen from liquid phase solution due to effect of high pressure [15].

APR is an attractive technique for production of hydrogen and alkane from renewable sources. By changing the process parameters, catalyst and feed, the reaction can be altered to the formation of hydrogen or alkanes [16].

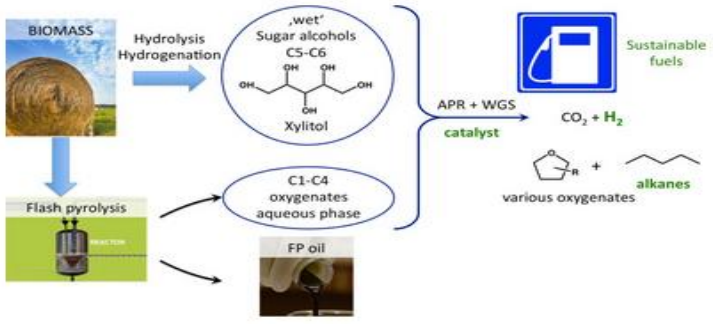


FIGURE 2.4 Process Flow of Fuel Production from Biomass Feedstock [17]

The reactions that involved in APR are illustrated in equation 1, 2 and 3 respectively [18].

Stoichiometric reaction of APR of glycerol:

$$C_3H_8O_3 + 3H_2O \longrightarrow 7H_2O + 3CO_2 \quad (1)$$

C-C/C-H bonds cracking of glycerol:

$$C_3H_8O_3 \longrightarrow 4H_2 + 3CO \quad (2)$$

Water – gas shift reaction:

$$CO + H_2O \longrightarrow CO_2 + H_2 \quad (3)$$

The further reaction of CO and/or with H_2 would lead to production of alkanes by methanation or Fisher-Tropsh reactions. The formation of alkanes will reduce the amount of hydrogen being produced [18].

2.4 Catalyst for Aqueous Phase Reforming

Yong Guo and co-workers had found out that high cost of platinum (Pt) makes the development of non precious catalyst such as nickel (Ni) based catalyst. Although skeletal Ni catalysts like Raney Ni showed a better stability in these catalysts but it lost about half of its initial activity. Ni-B amorphous alloy nanoparticle (AP Ni) catalyst was less active but more stable than Raney Ni. Besides, hydrogen produced from AP Ni catalyst was higher than Raney Ni [19].

According to Zhong Tang and friends, the platinum loaded NaY zeolite (Pt/NaY) catalysts have higher performance for the APR of methanol and ethanol than the conventional ɣ-alumina supported platinum (Pt/ɣ-Al_2O_3) catalyst [20].

TABLE 2.2 Comparison Study for Catalysts Used for APR of Glycerol

Catalyst	Reaction Conditions	Glycerol Conversion (%)	Product(s)
48wt% Ni/Al_2O_3 [21]	T = 260 °C P = Autogenous Pressure	95	Propanal, Acetone, 2-butanone, Ethanol 1-propanol, Cyclopentanone, 1-pentanol, 3-pentanol, 2,5-hexanedione, 2,3-dimethylcyclopentenone, 5-ethyldihydro-2-furanone,Phenol
17.4wt% Ni/Al_2O_3[18]	T = 230 °C P = 32 bar	15.8	Hydrogen, Carbon dioxide and Alkanes
Mg-Ni/Al_2O_3 [22]	T = 225 °C P = 30 bar	15	Hydrogen, Carbon dioxide, Methane, Propylenglycol, Ethylene glycol, Acetol and Ethanol.
Ni-B amorphous alloy catalyst (AP Ni) [19]	T = 225 °C P = 27.6 bar	29	Hydrogen and Methane
Ni/5wt%Cu [23]	T = 250 °C P = Autogenous Pressure	27	Lactic acid, Acetol and Acetaldehyde
Ni/Ce [24]	T = 270 °C P = Autogenous Pressure	21	Hydrogen, Carbon dioxide, Methane and Carbon monoxide
0.9wt%Pt/ɣ-Al_2O_3 [25]	T = 220 °C P = 25 bar	Not reported	Hydrogen
3wt%Pt/ Al_2O_3 [26]	T = 225 °C P = 29 bar	83	Hydrogen, Carbon dioxide, Methane, Ethane and Propane

1.49wt%Pt/ZrO2 and 1.44wt%Pt/MgO [27]	T = 225 °C P= 23 bar	20 - 26	Ethanol and Propanone
HZSM-5 HY Silica- Al_2O_3 ɣ- Al_2O_3 [28]	T = 350-500 °C P = 1 bar	80 - 100	Acetaldehyde, Acrolein and Formaldehyde Acetol

2.4.1 Bimetallic Catalyst

According to Pablo and co-worker, Ni catalyst without Cu showed higher conversion of glycerol compare to Ni catalyst with Cu due to low Ni dispersion. From the result, 60% is the maximum percentage of glycerol conversion at 270°C. Ni5Cu is the highest H_2 selectivity at temperature 250°C which is equal to 523 K, with the smallest amount of CO and CH_4. The least desirable temperature for Ni5Cu is at 270°C because almost total consumption of hydrogen and low conversion. Formation of methane is decreased due to addition of Cu in catalyst [29].

2.4.2 Effect of Adding Promoter into Catalyst

Based on report made by David L. Kinga and co-workers on effect of added rhenium, Re to Pt/C catalyst for APR of glycerol, they found that Re promoted catalysts show lower H_2 selectivity. The addition of Re gave dramatic impact in increasing the glycerol conversion. On the other hand, it also results higher alkanes and liquid phase product selectivity [30].

According to Kah Weng Siew and friends, La promotion enhances the metal dispersion on alumina support by decreasing the crystallite size. 2% of La into Ni-Al_2O_3 is the best composition for the reaction. 2%La-Ni-Al_2O_3 catalyst had gave optimum H_2 generation [31].The promotion of Mg and Ca in Ni/Al_2O_3 has give effect on the reaction of CO_2 and reforming CH_4. Besides, the promotions of alkaline

earth metals have high sensitivity of the method of catalyst preparation compare to lanthanide. It also weakening the Ni/Al_2O_3 interaction compares to unpromoted Ni/Al_2O_3 and it has reduce the difficulty of catalysts' reducibility [30,31].

2.5 Product and Intermediate

By referring chemical stoichiometric, the possible product that can produce from APR reaction is hydrogen. But with development of today technology, various potential products can be produced from glycerol. Figure 5 showed the possible chemicals can be produced from glycerol using diverse methods.

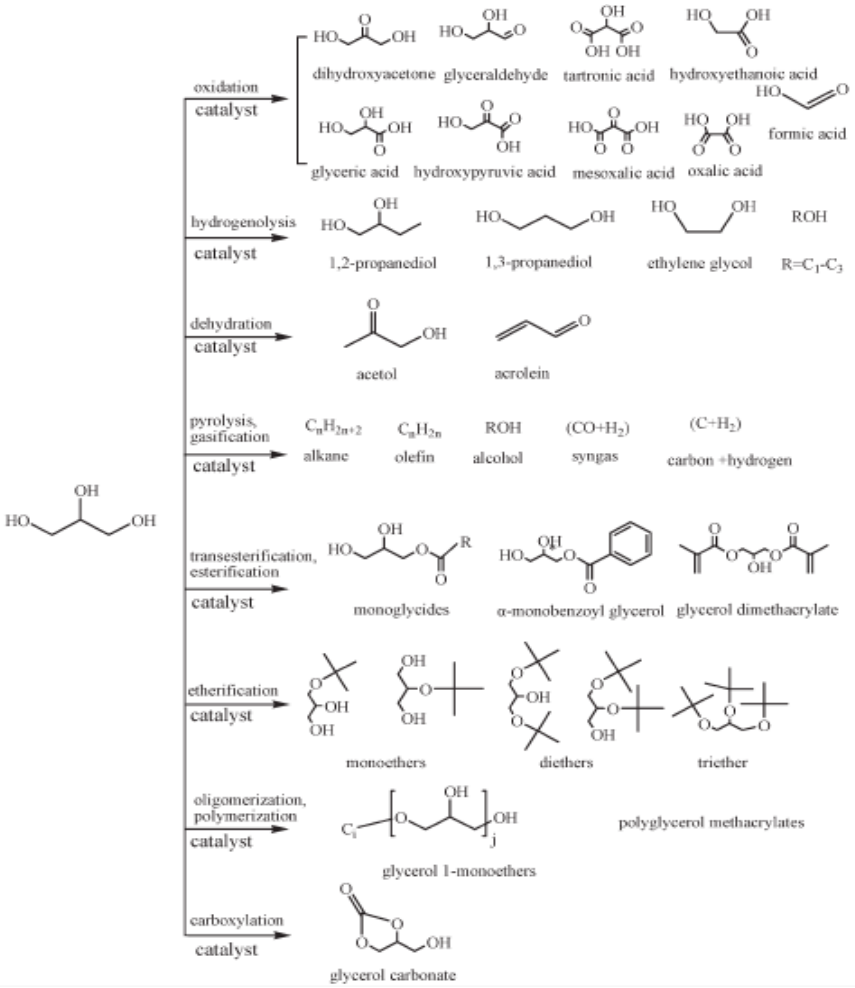


FIGURE 2.5 Process of Catalytic Conversion of Glycerol into Useful Chemicals [33].

In order to produce liquid products like methanol, ethanol, acetone, acetic acid, propanal 2,3 dihydroxyl, propylene glycol and diglycerol, glycerol should undergo dehydration and/or hydrogenation/dehydrogenation [25].

Cortright reported that the intermediates liquid products detected during aqueous phase reforming reactions are ethanol, 1,2-propanediol, methanol, 1-propanol, acetic acid, ethylene glycol, acetol, 2-propanol, propionic acid, acetone, propionaldehyde and lactic acid [26].

2.6 Effect of Concentration of Glycerol

Concentration of glycerol is one of the important parameter that can affect the selectivity and yield of the product.

Nianjun, L & co-workers said that the lower concentration of glycerol of 5 wt% can be reformed to produce with a higher yield than 10 wt%. The result of the research showed that higher concentration of feedstock will lower the yield of hydrogen but higher hydrogen selectivity [25].

According to Shyamsundar Ayalur Chattanathan research, at 5 % bio-oil concentration maximum hydrogen yield and minimum carbon monoxide yield were obtained. Hydrogen concentration was decrease with the increase of concentration and carbon monoxide concentration increase with concentration [34] .

2.7 Effect of Operating Temperature and Pressure

Nianjun Luo and co-workers said that higher reaction temperature and corresponding system pressure facilitated reforming process to produce higher hydrogen yield which is what would be expected as the process is endothermic. Lower reaction temperature would decrease the conversion of glycerine and higher temperature leads to more side reactions. However, a coupled condition of 493 K and 25 bar was seen to be the most suitable reaction condition for the liquid aqueous phase process [19].

According to Shyamsundar Ayalur Chattanathan, an increase in temperature resulted in increased hydrogen and carbon dioxide concentration while the carbon monoxide concentration was found to decrease with temperature [34].

2.8 Conclusion

Glycerol is valuable by-product that can be commercialized. Due to its potential, many researches had been done in order to reform glycerol to high value chemicals using several methods such as pryolysis, steam reforming, aqueous phase reforming, etc. Besides, the presence of catalysts and suitable operation conditions are needed to enhance the chemical reaction of glycerol that can produce assortment type of high value chemicals. Based on the literature study, the important points that can be use to references this project are the increase of glycerol concentration will decrease the production of hydrogen, high temperature and pressure will produce high hydrogen but lower the selectivity of hydrogen. The most significant element for this project is on the effect of addition promoter into the catalyst. Generally, the presence of promoter has given positive effect to the catalyst itself and the reaction.

CHAPTER 3

METHODOLOGY

3.1 Introduction

This chapter describes the experimental work conducted in this study. Figure 3.1 illustrated the project flow for the study.

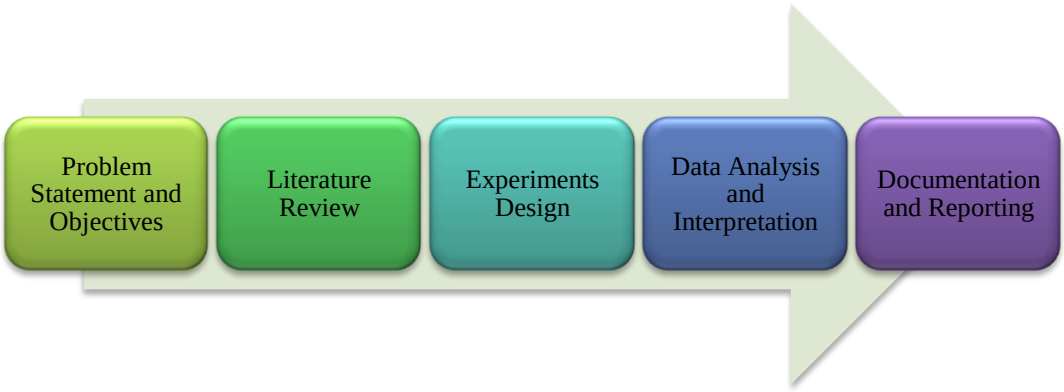


FIGURE 3.1 Flow of the Study

First and foremost, the researcher identified the purpose of this research project in order to set the direction of the study. Secondly, gathered as much as possible information from various trusted sources such as journals and websites. Third, identified matters that needed to be investigated, chemicals and equipments used and collected data from experiments. Fourth, researcher analyzed and interpreted the findings critically and made comparison with other literature readings that have been done. Finally, documented and reported the whole research project in detail and discussed recommendation or aspects that can be further improved in the future.

This study will be divided into three parts. The second part deals with Figure 7 illustrated the research activities.

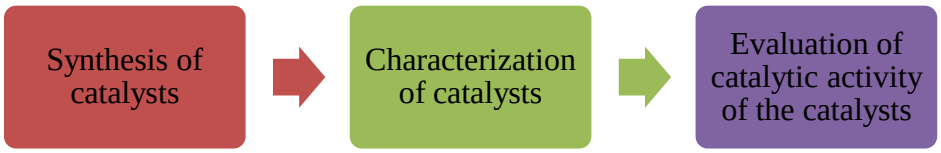


FIGURE 3.2 Flow Chart for Research Activities

For the first parts, the researcher synthesized nickel based catalysts promoted of bimetallic pair with calcium and magnesium salts through wetness impregnation method.

Second part is the part to determine the physiochemical properties of the synthesized catalysts through several characterization techniques such as SEM, XRD and BET analysis.

Finally, these catalysts were evaluated in a reactor system to test their performance in APR reaction.

3.2 Gantt Chart & Key Milestones for FYP

TABLE 3.1 Project Gantt Chart

	FYP 1														FYP 2													
Detail / Week	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
Critical literature review of aqueous phase reforming, promoted catalysts and incipient wetness impregnation method	■																												
Requisition of chemicals and laboratory apparatus					■	■	■																						
Synthesis of catalyst										■	■	■	■	■	■	■	■	■	■	■									
Characterization of catalysts and evaluation of catalytic activity of the catalysts															■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
Submission of Progress Report																						●							
Pre-Sedex																									●				
Submission of Draft Final Report																										●			
Submission of Dissertation (soft bound)																											●		
Submission of Technical Paper																											●		
Viva																												●	
Submission of Project Dissertation (Hard Bound)																													●

Indicator: ■ Duration Interval ● Key Milestones

3.3 Chemicals and Equipment

TABLE 3.2 List of Chemicals Equipment

Chemicals	Quantity	Purpose
Gamma Alumina	1 kg	Catalyst Synthesis
Nickel Nitrate Hexahydrate	500 g	Catalyst Synthesis
Magnesium Nitrate Hexahydrate	500 g	Catalyst Synthesis
Calcium Chloride Dehydrate	500 g	Catalyst Synthesis
Glycerol	1 Litre	Catalytic Activity Test
n-Hexane	50 ml	Gas Chromatography Standard
Propanol	50 ml	Gas Chromatography Standard
Ethylene glycol	50 ml	Gas Chromatography Standard
Ethanol	50 ml	Gas Chromatography Standard
1,3 - Propanediol	50 ml	Gas Chromatography Standard
Propionaldehyde	50 ml	Gas Chromatography Standard
Propylene Glycol	50 ml	Gas Chromatography Standard
0.005 M Sulphuric Acid	1 Litre	Mobile Phase for High Performances Liquid Chromatography
PREMEX Autoclave Reactor	1	Catalytic Activity Test
Beaker 250 ml	5	Catalyst Synthesis
Beaker 500 ml	2	Catalyst Synthesis
Crucible	5	Catalyst Synthesis
Hot Plate Stirrer	2	Catalyst Synthesis
Spatula	1	Catalyst Synthesis
Magnetic Bar	2	Catalyst Synthesis

3.4 Synthesis of Catalysts

The propose method to prepare the catalysts is incipient wetness impregnation (IWI). Impregnation is the most common procedure to spread the catalytic species within the carrier. For IWI, the maximum liquid uptake is referring to the pore volume of the carrier. Then the precursor salt will be dissolved in an amount of liquid similar to the pore volume of the carrier [35].

For this project thirteen (13) samples with different composition metal loading are prepared using nickel nitrate hexahydrate $Ni(NO_3)_2.6H2O$, magnesium nitrate hexahydrate $Mg(NO_3)_2.6H2O$ and calcium chloride dehydrate $CaCl_2.2H2O$ on gamma alumina ɣ-Al_2O_3 support.

TABLE 3.3 Composition of Catalysts

Sample	Composition of Al_2O_3:Ni:Ca:Mg	Sample	Composition of Al_2O_3:Ni:Ca:Mg
10% Ni/ɣ-Al_2O_3	90:10:0:0	3% Mg, 10% Ni/ ɣ-Al_2O_3	87:10:0:3
0.5% Ca, 10% Ni/ɣ-Al_2O_3	89.5:10:0.5:0	5% Mg, 10% Ni/ ɣ-Al_2O_3	85:10:0:5
3% Ca, 10% Ni/ ɣ-Al_2O_3	87:10:3:0	7% Mg, 10% Ni/ ɣ-Al_2O_3	83:10:0:7
5% Ca, 10% Ni/ ɣ-Al_2O_3	85:10:5:0	10% Mg, 10% Ni/ ɣ-Al_2O_3	80:10:0:10
7% Ca, 10% Ni/ ɣ-Al_2O_3	83:10:7:0	0.5% Ca + Mg, 10% Ni/ ɣ-Al_2O_3	89:10:0.5:0.5
10% Ca, 10% Ni/ ɣ-Al_2O_3	80:10:10:0	5.0% Ca + Mg, 10% Ni/ɣ-Al_2O_3	80:10:5:5
0.5% Mg, 10% Ni/ɣ-Al_2O_3	89.5:10:0:0.5		

The procedure to synthesis Ni/ɣ-Al_2O_3 catalyst with promoter Ca/Mg using incipient wetness impregnation method:

1. Gamma alumina is calcined in furnace for overnight at 500°C.

FIGURE 3.3 Calcined Al2O3

2. Nickel nitrate hexahydrate salt is diluted in distilled water to become aqueous solution.

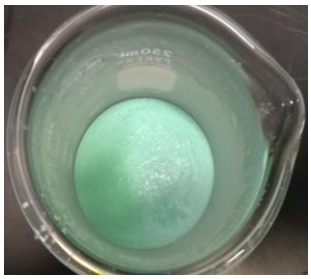
FIGURE 3.4 Nickel Salt Solution

3. Calcined Al_2O_3 is mixed with nickel nitrate hexahydrate solution and stirred it for 4 hours.

FIGURE 3.5 Mixture of Nickel Salt and Alumina

4. The mixture is dried in oven for overnight.

Addition of Calcium



Addition of Magnesium

FIGURE 3.6 After Drying Process

5. The powder is calcined in furnace for 16 hours.
6. Lastly, the powder is sieved to 212 mm of particle size using sieve.

(a)

(b)

FIGURE 3.7 (a) ɣ-Al2O3 before Synthesized, (b) ɣ-Al2O3 after Synthesized

7. For promoted or pair catalysts preparation, the calcium and magnesium salt is added into nickel nitrate hexahydrate solution and step 3 to 5 is repeated.
8. The catalyst is reduced in Temperature Programmed Desorption; Reduction & Oxidation (TPDRO) instrument.

FIGURE 3.8 TPDRO Instrument [36]

3.5 Characterization of Catalysts

The purpose of characterization of catalyst is to determine the physiochemical properties of the synthesized bimetallic catalysts using a few techniques such as BET, SEM and XRD.

TABLE 3.4 List of Characterization Techniques

Method of Characterization	Equipment	Functions
X-Ray Diffraction (XRD)	 [37]	To discover species present and degree of crystallinity [23].
Brunauer-Emmett-Teller (BET) analysis	 [38]	To recognize specific surface area [39].

Scanning Electron Microscope (SEM)		To produce high resolution images of shapes of objects and to show spatial variations in chemical composition
Field Emission Scanning Electron Microscopy (FESEM)	 [40]	To know the morphology of the catalysts [20].
Temperature-programmed reduction (TPR)	 [41]	To distinguish the reducible species existence, their interaction and degree of reducibility [23]

3.6 Evaluation of Catalytic Activity of the Catalysts

The catalysts will be evaluated in PREMEX autoclave reactor to test their performance in Aqueous Phase Reforming. This reactor can hit to 100 bar with 250°C maximum working temperature which is suit to be used for APR reaction.

FIGURE 3.9 PREMEX Autoclave Reactor [42]

3.6.1 Glycerol Solution Preparation

Glycerol is diluted using distilled water. The required concentration of glycerol is 1 wt% instead of 100 wt% of glycerol in 500 ml of glycerol solution. The formula used to dilute the glycerol is:

Glycerol needed,

$$\frac{1\ \%}{100\ \%} \times 500\ ml = 5\ ml \tag{4}$$

Distilled water needed,

$$500\ ml - 5\ ml = 495\ ml \tag{5}$$

The procedure of preparation of glycerol solution is:

1. 5 ml of pure glycerol is measured using measuring cylinder.
2. Then 495 ml of distilled water also is measured.
3. Both liquids are mixed together in a beaker and stirred well using spatula.

3.6.2 Experiment Procedure

All the operating parameters such as temperature, pressure and concentration of glycerol are fixed but the type of catalyst is manipulated variable.

TABLE 3.5 Variables for the Experiment

Constant variables	Temperature: 230°C Pressure: 20 bar Speed of Rotation: 450 rpm Concentration of Glycerol: 1 wt%
Manipulated variable	Type of Catalysts
Responding variable	Type of Value Added Chemicals Produced

The reaction of aqueous phase reforming is done in PREMEX Autoclave Reactor in the condition stated above. The experiment procedures for APR of glycerol are:

1. 1 g of catalyst is weighed using weight balance.
2. Glycerol solution and catalyst are put together in the reactor.
3. Autoclave reactor is switch on.
4. Temperature; 230°C, pressure; 20 bar and speed of rotation; 450 rpm are set.
5. After 30 minutes, the reforming liquid sample is been token out from discharge vessel.
6. The liquid is now ready to been analyzed using High Performance Liquid Chromatography (HPLC) to know what are the value added chemicals formed.
7. All steps are repeated using different catalyst.

3.6.3 Instrument Method for HPLC

- Injection Volume: 30 µL
- Flow rate: 0.6 mL/min
- Pressure: 48 bar
- Temperature: 30 ˚C
- Mobile Phase: 0.005M of H_2SO_4
- Detector: UV
- Column: Eclipse XDB C18, 5 µm, 4.6 x 150 mm, Agilent
- Runtime: 35 minutes
- Signal: 215 nm and above

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

For this chapter, the results of catalysts characterization and reaction studies will be presented and discussed. The results are interpreted in terms of physical characteristics and the catalytic activity of the catalysts.

4.2 Catalyst Formulation

Thirteen samples of different compositions were prepared based on the calculation shown in APPENDIX 1. Table 4.1 shows the composition of the thirteen samples.

TABLE 4.1 Composition of Catalysts

Sample	Composition of Al_2O_3:Ni:Ca:Mg	Sample	Composition of Al_2O_3:Ni:Ca:Mg
10% Ni/ɣ-Al_2O_3	90:10:0:0	3% Mg, 10% Ni/ ɣ-Al_2O_3	87:10:0:3
0.5% Ca, 10% Ni/ɣ-Al_2O_3	89.5:10:0.5:0	5% Mg, 10% Ni/ ɣ-Al_2O_3	85:10:0:5
3% Ca, 10% Ni/ ɣ-Al_2O_3	87:10:3:0	7% Mg, 10% Ni/ ɣ-Al_2O_3	83:10:0:7
5% Ca, 10% Ni/ ɣ-Al_2O_3	85:10:5:0	10% Mg, 10% Ni/ ɣ-Al_2O_3	80:10:0:10
7% Ca, 10% Ni/ ɣ-Al_2O_3	83:10:7:0	0.5% Ca + Mg, 10% Ni/ ɣ-Al_2O_3	89:10:0.5:0.5
10% Ca, 10% Ni/ ɣ-Al_2O_3	80:10:10:0	5.0% Ca + Mg, 10% Ni/ɣ-Al_2O_3	80:10:5:5
0.5% Mg, 10% Ni/ɣ-Al_2O_3	89.5:10:0:0.5		

4.3 Characterization of Catalysts

For characterization, only few of the catalysts were being sent to test because more or less the pattern of results will be same due to small different composition of metal loading which are calcium and magnesium.

4.3.1 X-Ray Diffraction (XRD)

The purpose of using XRD is to detect the present of Ni and other metals like Ca and Mg in ɣ-Al_2O_3 support. By comparing the XRD spectrum of Al2O3 and different composition of catalysts, the present of those metals can be traced.

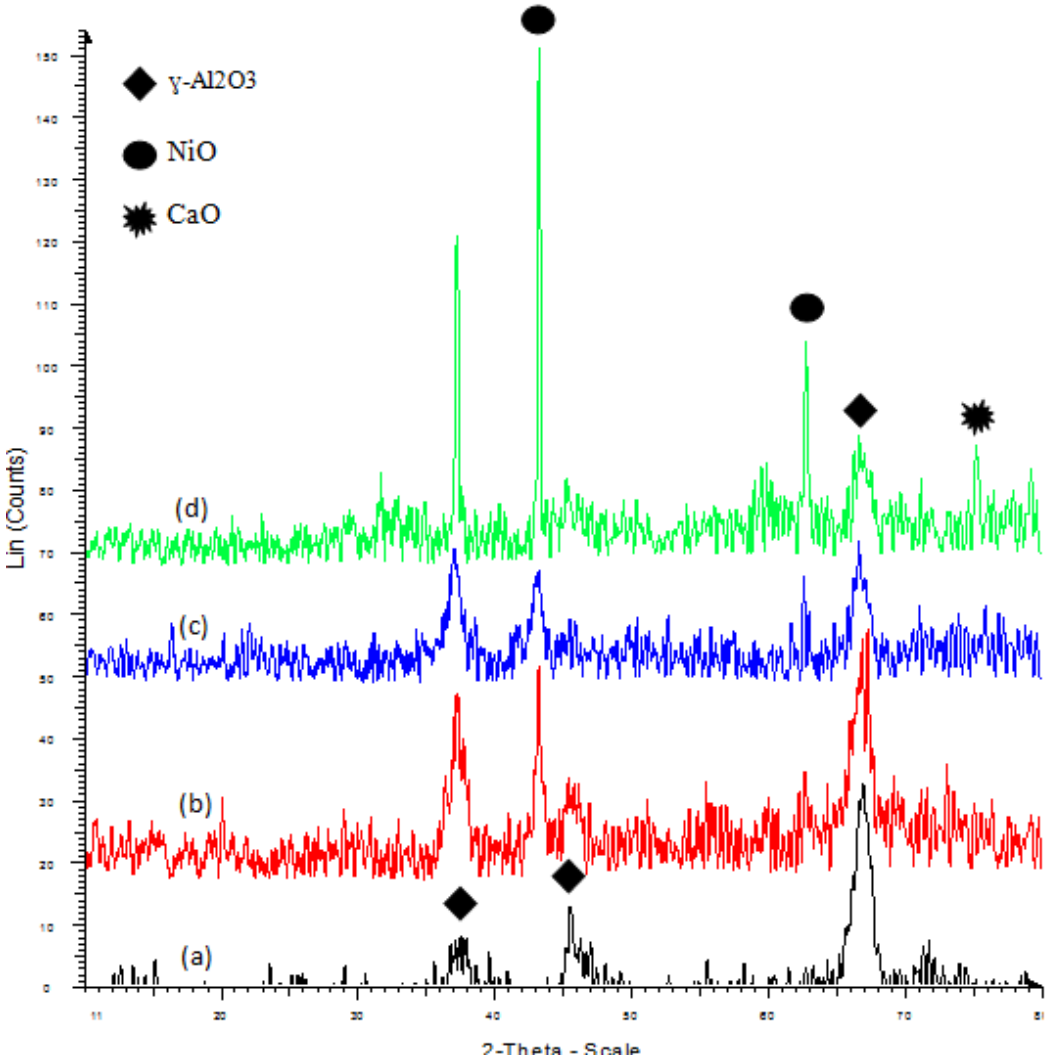


FIGURE 4.1 XRD Patterns for (a) ɣ-Al2O3, (b) 10%Ni/ɣ-Al2O3, (c) 0.5%Ca, 10%Ni/ɣ-Al2O3, (d) 3.0%Ca, 10%Ni/ɣ-Al2O3

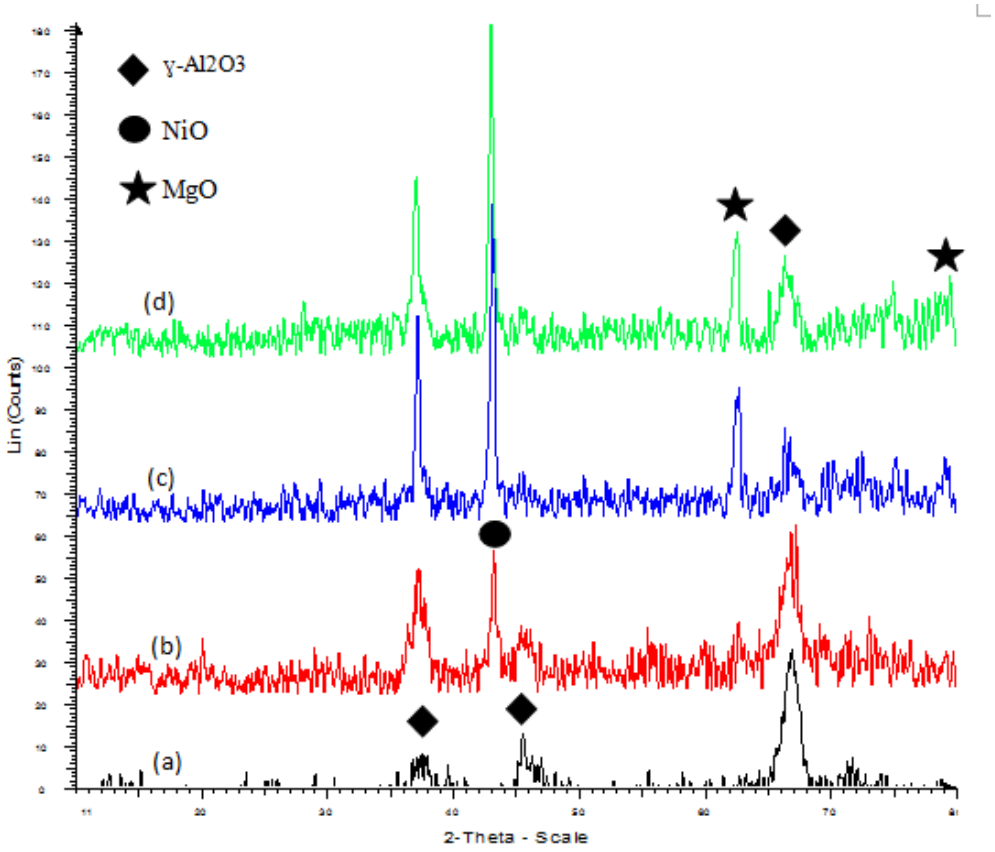


FIGURE 4.2 XRD Patterns for (a) ɣ-Al2O3, (b) 10%Ni/ɣ-Al2O3, (c) 0.5%Mg, 10%Ni/ɣ-Al2O3, (d) 3.0%Mg, 10%Ni/ɣ-Al2O3

From Figure 4.1 and 4.2, the characterization peaks of crystalline peaks of Al_2O_3 can be seen at 37.5°, 45.5° and 67.3° [43]. Besides, diffraction lines of crystalline phases of NiO were observed at 19.5°, 43.2° and 63° [43]. Characterization peak of crystalline peak of CaO was seen at 76° [44]. While diffraction lines of crystalline phases of MgO were observed at 62.5° and 79°. The addition of calcium and magnesium increased the intensity of the catalyst; it shows that there is good formation of crystalline structure. According to Shaobin Wang & Lu (1997), the sharper the peak shows the lower dispersion nickel on the catalysts. Besides, there is study from Chen et.al [45] stated that used of nickel nitrate salts in preparation of Ni – alumina will give high dispersion and large surface area of supported nickel oxide. Compare to other study such as Rusiene et.al [46], even though used different temperature for heat treatment, the peak formed at XRD more less is same. This shows that each element still have the same degree of crystallinity even it was treated differently.

4.3.2 Brunauer, Emmett and Teller (BET) Surface Area

The purpose of doing BET test is to measure the surface area, pore volume and pore size through N_2 physical adsorption equipment.

TABLE 4.2 Textural Properties of Catalysts

Sample	BET Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Size (nm)
ɣ-Al_2O_3	135.7381	0.235422	6.93753
10%Ni/ ɣ-Al_2O_3	107.2489	0.193949	7.23359
0.5% Ca,10%Ni/ ɣ-Al_2O_3	104.8699	0.185242	7.06559
3.0% Ca,10%Ni/ ɣ-Al_2O_3	55.0590	0.117819	6.6552
7.0% Ca,10%Ni/ ɣ-Al_2O_3	82.4003	0.153882	6.2955
0.5% Mg,10%Ni/ ɣ-Al_2O_3	106.0933	0.190004	7.16367
3.0% Mg,10%Ni/ ɣ-Al_2O_3	87.7006	0.148206	6.0892
7.0% Mg,10%Ni/ ɣ-Al_2O_3	94.8726	0.158562	5.5883
0.5% Ca + Mg,10%Ni/ ɣ-Al_2O_3	79.9009	0.163518	6.6680
5.0% Ca + Mg,10%Ni/ ɣ-Al_2O_3	67.9107	0.116565	5.6477

From the results given in Table 4.2, Al_2O_3 has the largest surface area and pore volume compare to others but it quite small pore size. The addition of Ca and Mg into 10% Ni/ɣ-Al_2O_3 catalyst decreased the surface area, pore volume and pore size due to the plugging of metals in the pores. The study from Kah et.al [31] also gained the same result with this study which are the higher amount of La that act as promoter, more pores were covered. But the addition of Ca into Ni based catalyst result smaller BET surface are, pore volume and size rather than addition of Mg into Ni based catalyst.

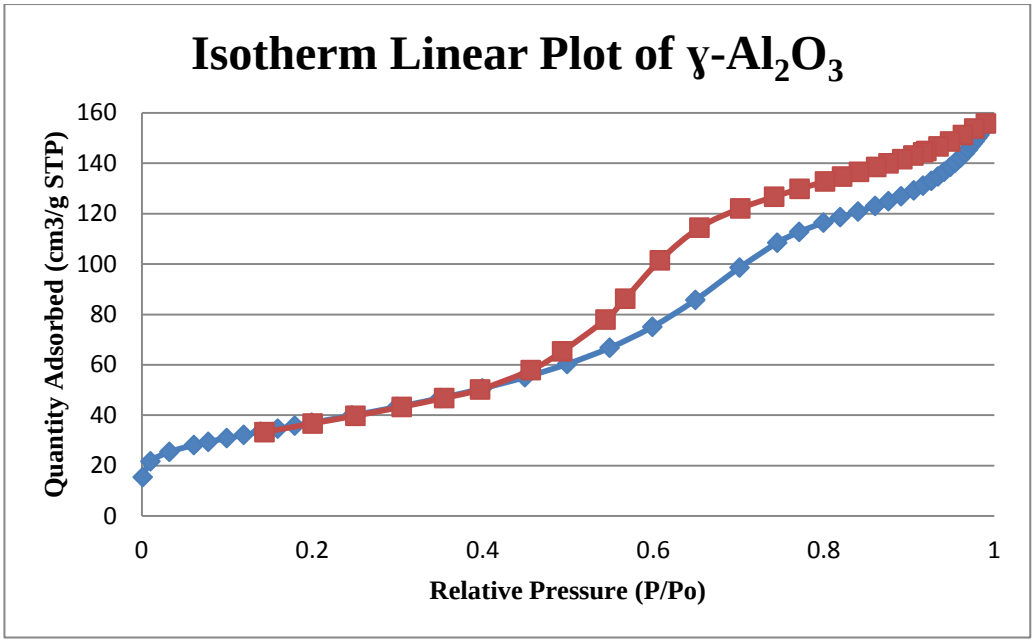


FIGURE 4.3 Isotherm Linear Plot of ɣ-Al_2O_3

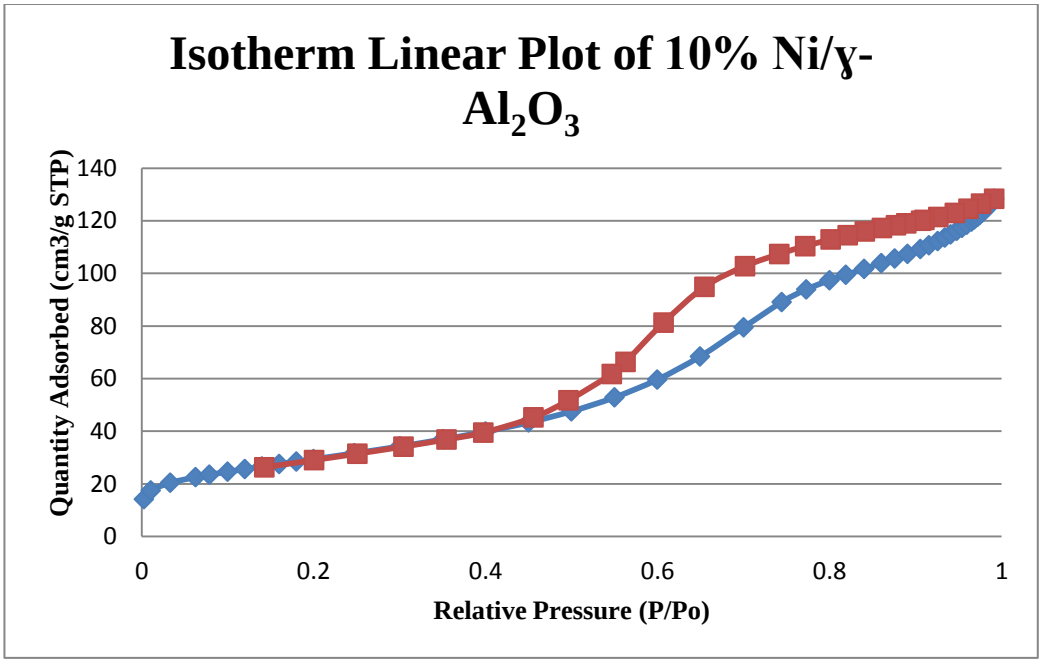
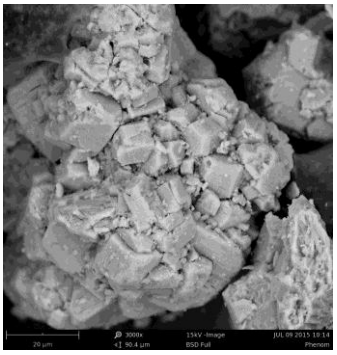


FIGURE 4.4 Isotherm Linear Plot of 10%Ni/ ɣ-Al_2O_3

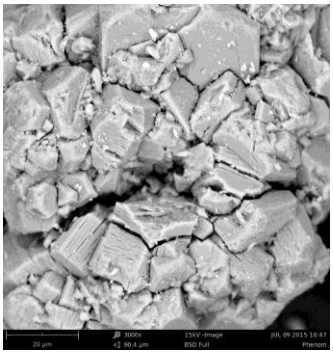
From the graphs in Figure 4.3 and 4.4, all catalysts follow type IV isotherm which are for mesoporous materials like mesoporous alumina. The other graphs can be seen in Appendix II. At the initial part of this isotherm which is the lower pressure part of the graph can be associated to monolayer-multilayer adsorption which is same with the type II isotherm. The occurrence capillary condensation can be correlated with the most characteristic feature of the type IV isotherm which is the hysteresis loop. The complete pore filling can be indicated from the limiting uptake over a range of high P/Po result in the isotherm [47].

4.3.3 Scanning Electron Microscopy (SEM)

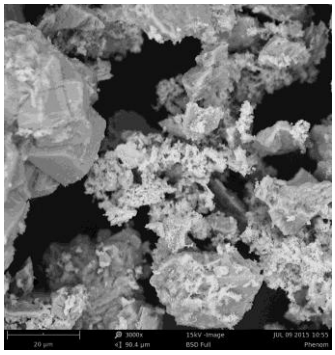
Scanning Electron Microscopy (SEM) was used to find out the morphology of the catalyst. SEM – EDS analysis was carried out to know the distribution of elements and chemical composition present in the catalyst.



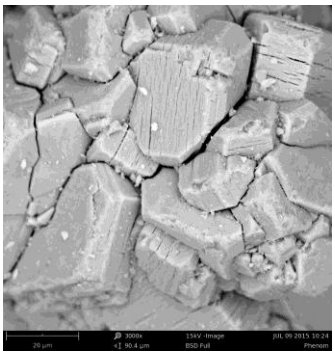
10% Ni/ɣ-Al_2O_3



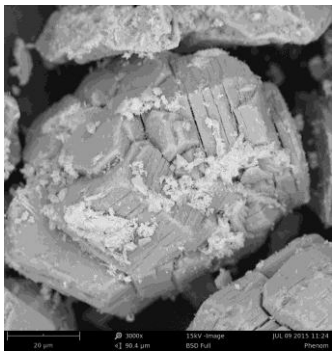
0.5% Ca + Mg, 10% Ni/ɣ-Al_2O_3



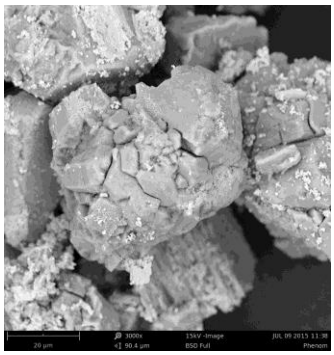
5% Ca + Mg, 10% Ni/ɣ-Al_2O_3



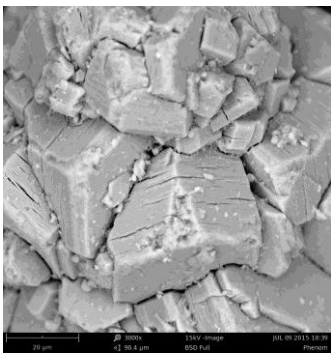
0.5% Ca, 10% Ni/ɣ-Al_2O_3



3% Ca, 10% Ni/ɣ-Al_2O_3

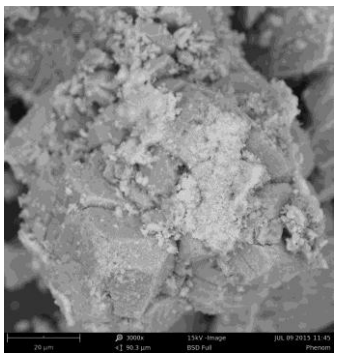


7% Ca, 10% Ni/ɣ-Al_2O_3



0.5% Mg, 10% Ni/ɣ-Al_2O_3

3% Mg, 10% Ni/ɣ-Al_2O_3



7% Mg, 10% Ni/ɣ-Al_2O_3

FIGURE 4.5 SEM Images at 20 µm Magnification

TABLE 4.3 SEM-EDS Elemental Analyses for Catalysts

Catalyst	Composition (%)
1 (10% Ni/ɣ-Al_2O_3)	Aluminium – 46.0 Oxygen – 37.6 Nickel – 16.4
2 (0.5% Ca, 10% Ni/ ɣ-Al_2O_3)	Aluminium – 46.3 Oxygen – 40.7 Nickel – 13.0
3 (0.5% Mg, 10% Ni/ ɣ-Al_2O_3)	Aluminium – 40.7 Oxygen – 49.6 Nickel – 9.2 Magnesium – 0.6
4 (3% Ca, 10% Ni/ ɣ-Al_2O_3)	Aluminium – 43.6 Oxygen – 34.7 Nickel – 17.1 Calcium – 4.6
5 (3% Mg, 10% Ni/ ɣ-Al_2O_3)	Aluminium – 33.3 Oxygen – 40.1 Nickel – 22.2 Magnesium – 4.0
6 (7% Ca, 10% Ni/ ɣ-Al_2O_3)	Aluminium – 43.2 Oxygen – 41.8 Nickel – 7.7 Calcium – 7.8
7 (7% Mg, 10% Ni/ ɣ-Al_2O_3)	Aluminium – 33.6 Oxygen – 29.17 Nickel – 27.0 Magnesium – 9.7
8 (0.5% Ca + Mg, 10% Ni/ ɣ-Al_2O_3)	Aluminium – 44.1 Oxygen – 36.4 Nickel – 18.4 Calcium – 0.7 Magnesium – 0.5

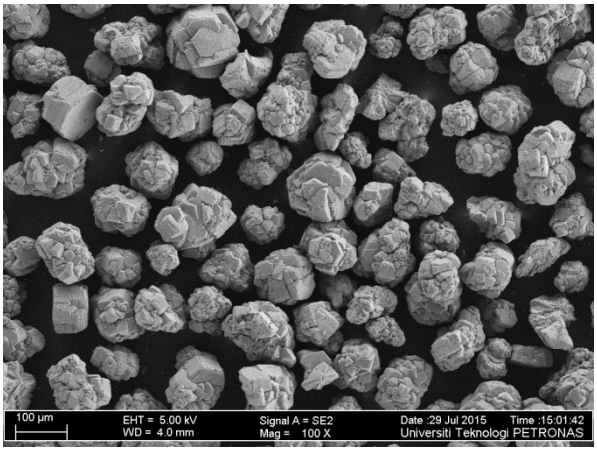
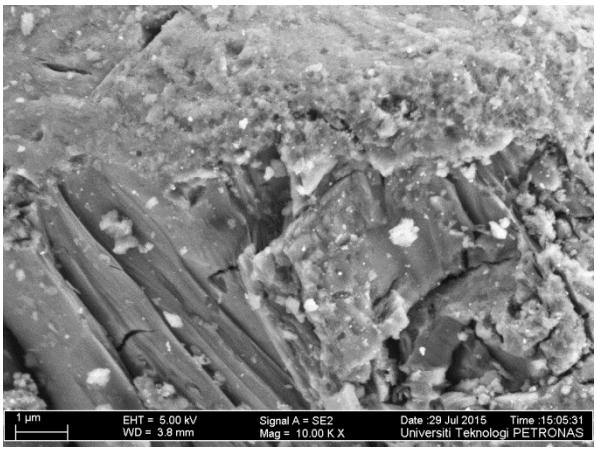
9 (5% Ca + Mg, 10% Ni/ ɣ-Al_2O_3)	Aluminium – 54.2 Oxygen – 25.8 Nickel – 10.6 Calcium – 4.6 Magnesium – 4.8

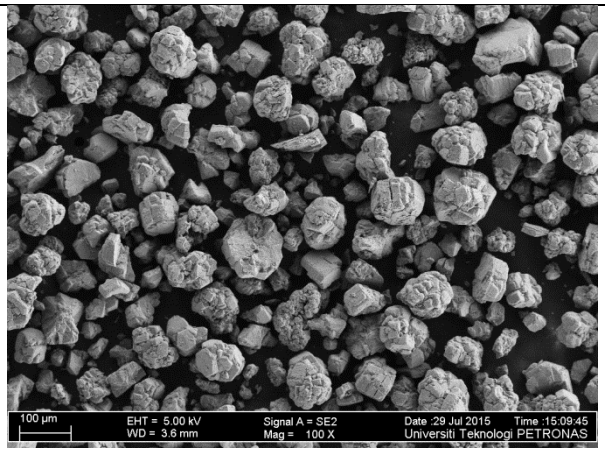
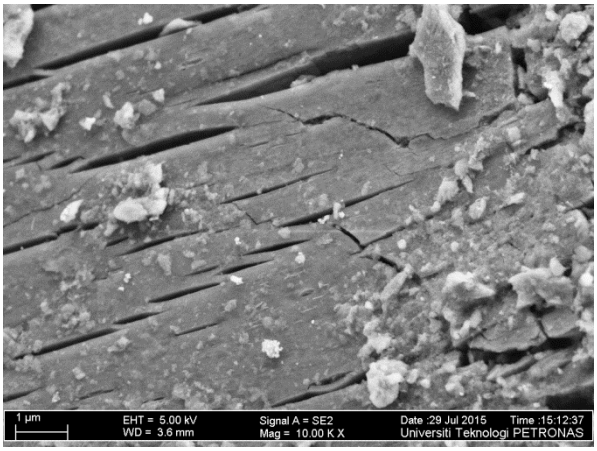
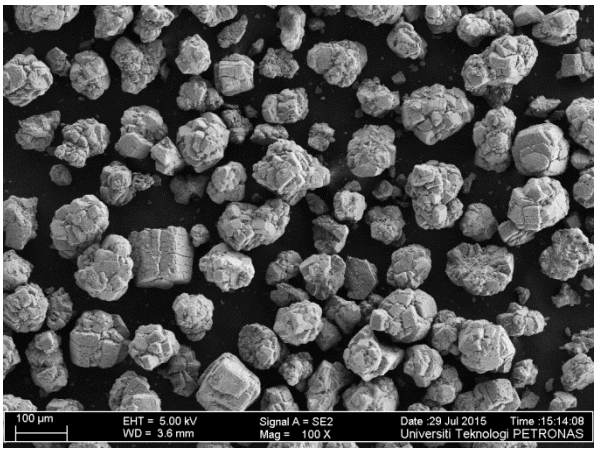
The crystal growth on large particles of alumina can be seen clearly in all samples. The metals such as nickel, calcium and magnesium particles are visibly dispersed on the support. But for the promoter catalysts (0.5% Ca and 0.5% Mg), the promoter particles cannot be seen clearly due to small amount used. Besides, the reducing surface area as a result of increasing amount of calcium or magnesium into the catalyst can be seen in the image.

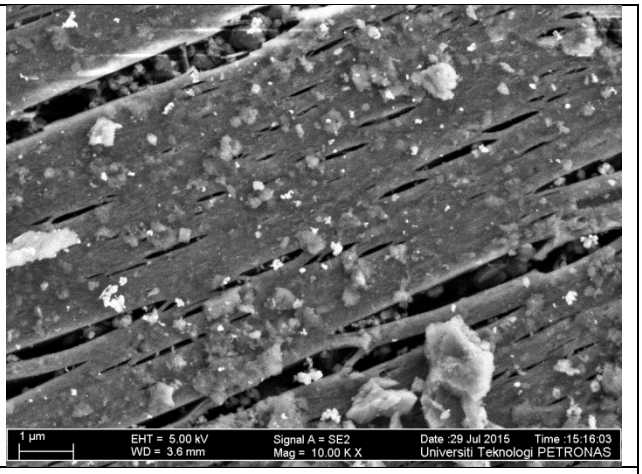
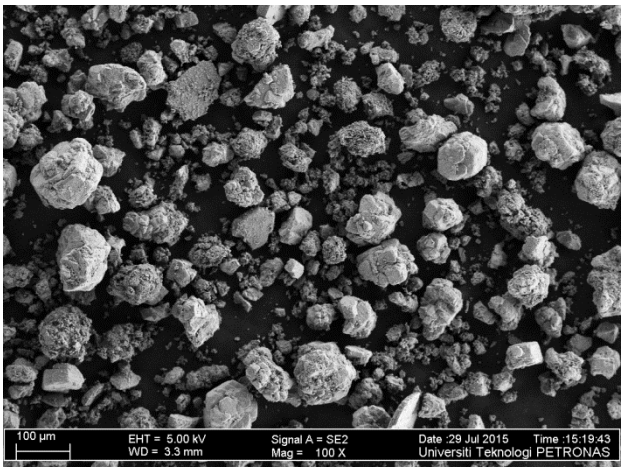
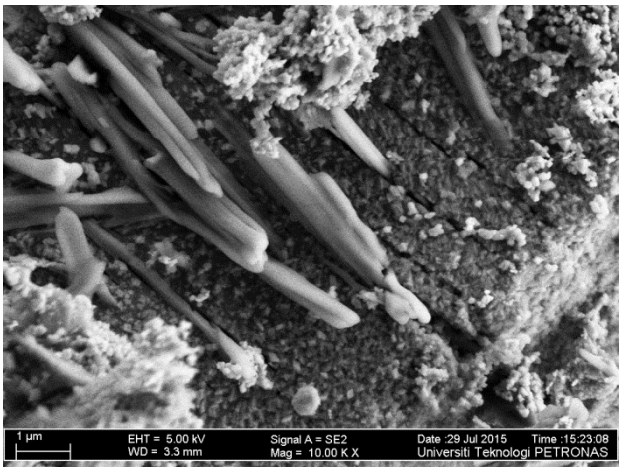
4.3.4 Field Emission Electron Microscope (FESEM)

From FESEM-EDX analysis, the surface properties of alumina supported by Ni, Ca/Mg catalyst prepared by incipient wetness impregnation method can be identified. Only few sample were been characterized with the aim to compare with the results from SEM test.

TABLE 4.4 Results from FESEM-EDX

Catalyst	Composition (%)	Image (100 X, 10 KX)
(10% Ni/ɣ-Al_2O_3)	Aluminium – 41.7 Oxygen – 48.6 Nickel – 9.72	 

0.5% Mg, 10% Ni/ɣ-Al_2O_3	Aluminium – 40.7 Oxygen – 48.0 Nickel – 10.6 Magnesium 0.66	 
0.5% Ca + Mg, 10% Ni/ɣ-Al_2O_3	Aluminium – 37.7 Oxygen – 47.0 Nickel – 12.3 Magnesium 0.86 Calcium – 1.5	

		
5.0% Ca + Mg, 10% Ni/ɣ-Al_2O_3	Aluminium – 23.7 Oxygen – 37.6 Nickel – 24.2 Magnesium – 7.0 Calcium – 4.1	 

By compared results from FESEM and SEM, the amount of calculated elements and the elements' value obtained from the experiment were in good agreement. Even though, the value is not exactly the same but the value of element still in the acceptable range. This results show the elements were well dispersed using incipient wetness impregnation method.

4.3.5 Temperature Programmed Reduction (TPR)

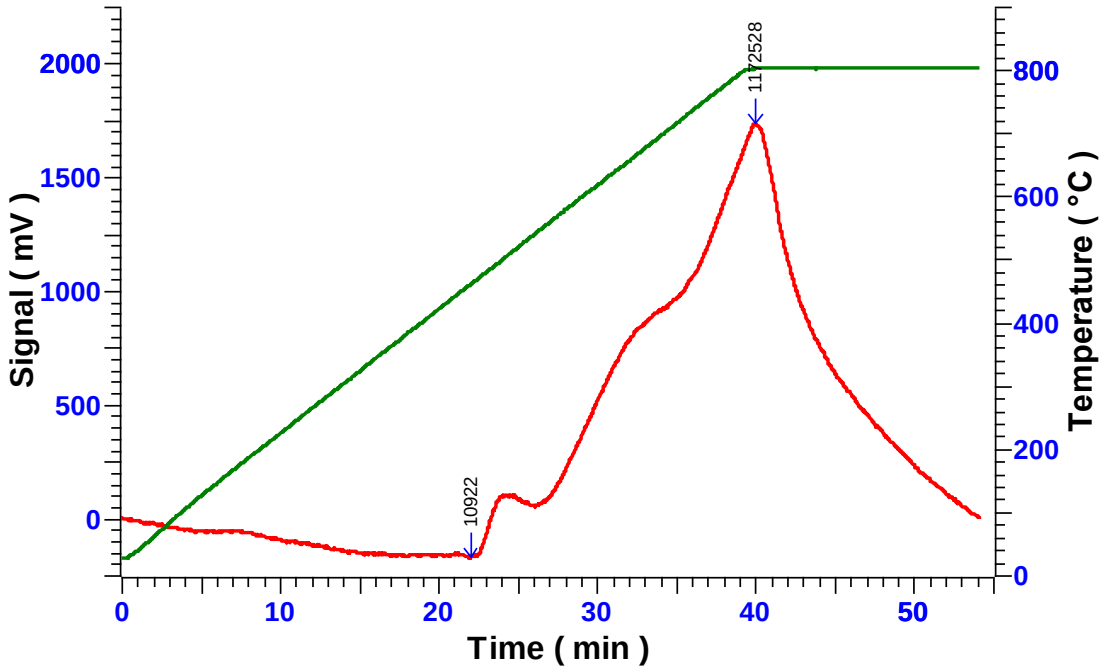


FIGURE 4.6 TPR Profile for 10% Ni/ɣ-Al_2O_3

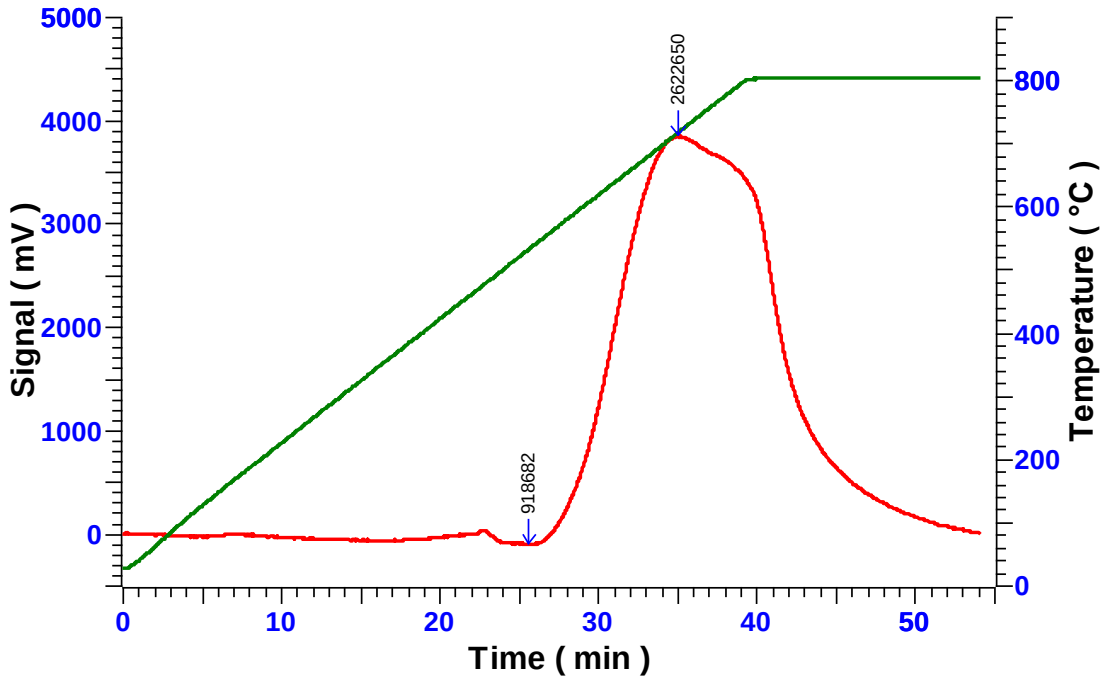


FIGURE 4.7 TPR Profile for 0.5% Ca, 10% Ni/ɣ-Al_2O_3

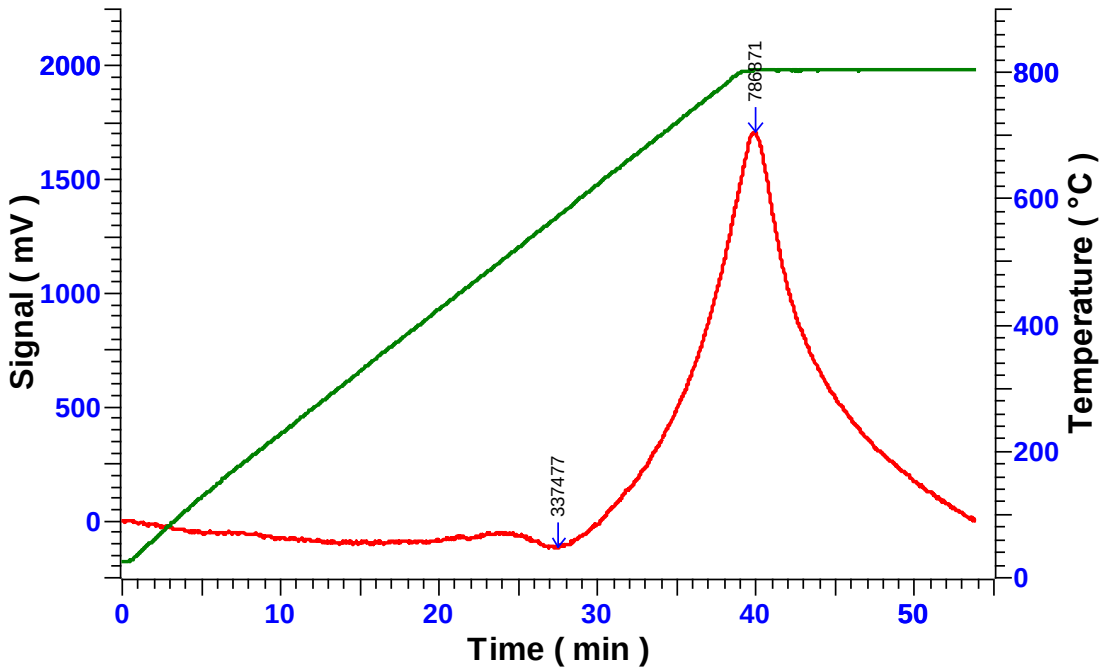


FIGURE 4.8 TPR Profile for 3.0% Mg, 10% Ni/ɣ-Al2O3

From the TPR profiles above, even though composition of calcium and magnesium different for every sample but it still have same reduction's temperature which is 660°C because the samples have same amount of nickel loading. The fundamental of supporting nickel at high surface area ceramic such as alumina is to increase the surface are of nickel itself. Then, there will be interaction between nickel and support but it does depend on the chemical and physical properties of the support. The nickel-support interaction can be characterized using the reducibility of nickel [48]. Metal loading and calcinations temperature are the factors that influencing the reduction. For this study, the percentage of nickel loading which is 10wt% and the calcinations temperature which is 500°C are fixed, that why the samples have same reduction temperature.

4.4 Aqueous Phase Reforming Performance Glycerol

4.4.1 High Performance Liquid Chromatography (HPLC) results

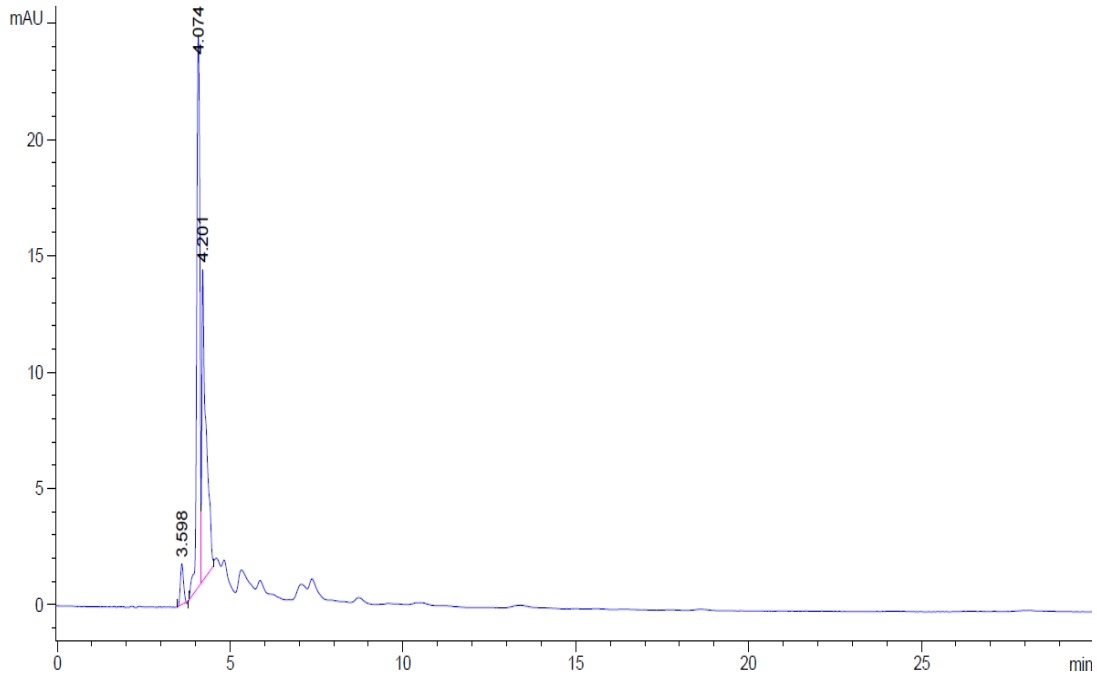


FIGURE 4.9 HPLC Result of 1wt% Glycerol Solution

In order to know the effect of catalyst's presence in APR reaction, first experiment is run only used 1wt% glycerol solution without any catalyst. From the HPLC result obtained above, it can be deduced that the highest peak, 23.80381 mAU and second highest peak, 13.45872 mAU belong to glycerol. The retention time for glycerol is 4.074 minutes and 4.201 minutes. Thus, from this result it shows that APR of glycerol cannot perform unless there is catalyst presence. Yet, there is one unforeseen peak with retention time 3.598 minutes formed which the peak does not appear in the result of standard solution which can be seen in Appendix IV.

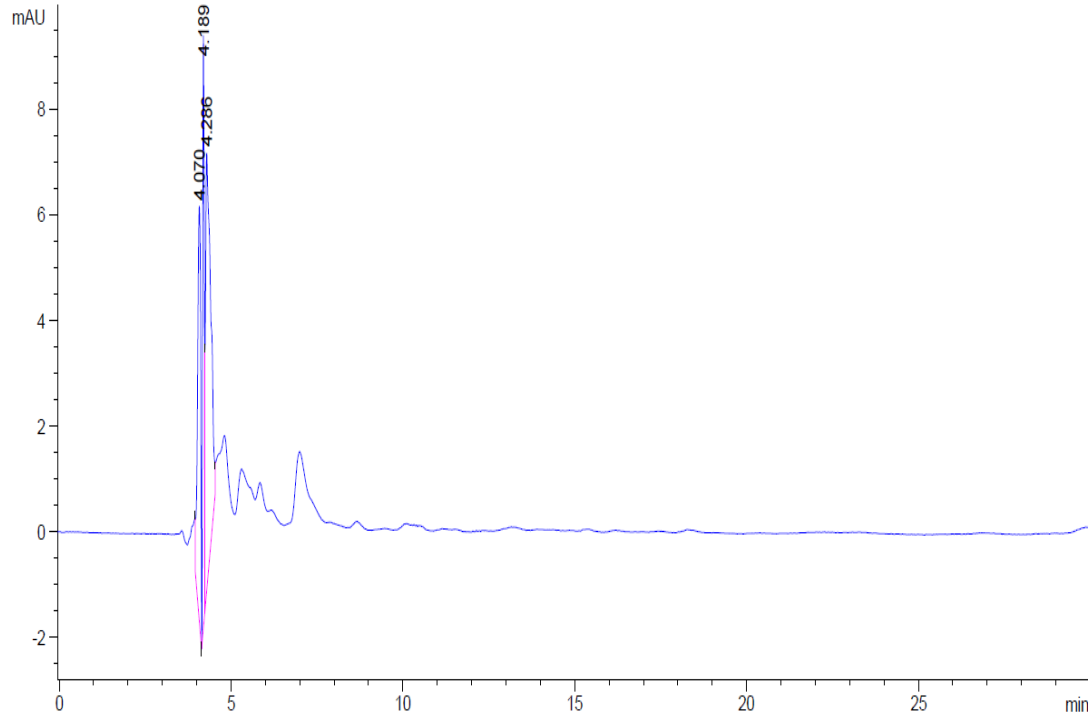


FIGURE 4.10 HPLC Result Used 10%Ni/ ɣ-Al2O3

From the result, the highest peak which is 11.29900 mAU with the retention time 4.189 minutes belongs to propionaldehyde. Followed by, the second highest peak; 8.34550 mAU with the retention time 4.286 minutes belongs to ethanol. The lowest peak with height 7.82840 mAU can be assumed belongs to glycerol. The retention time is 4.070 minutes. The presence of glycerol in this peak shows that the 1wt% glycerol solution is not fully converted.

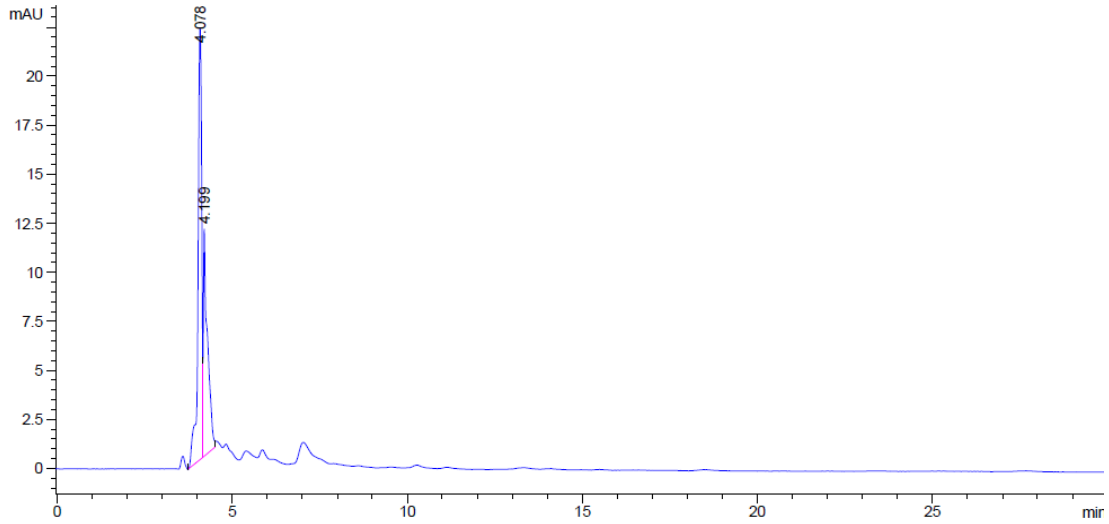


FIGURE 4.11 HPLC Result Used 0.5% Ca, 10%Ni/ ɣ-Al2O3

Based on the figure above, there are two peaks formed. Both peaks with retention time 4.078 minutes and 4.199 minutes fit in to glycerol. From this result, it shows that there is no conversion of glycerol.

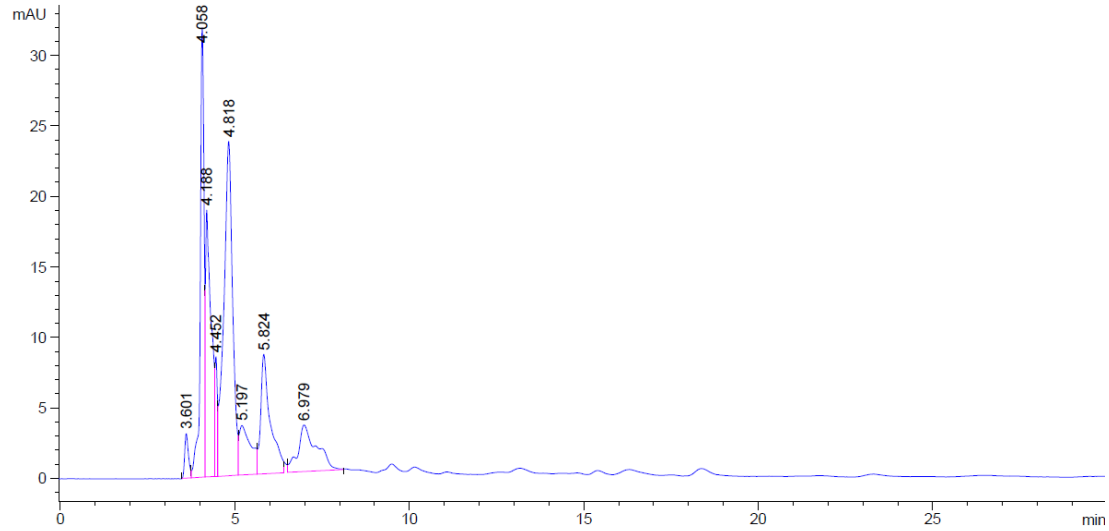


FIGURE 4.12 HPLC Result Used 3.0%Ca, 10%Ni/ ɣ-Al2O3

There are eight peaks formed in figure above. Yet, only three peaks similar with standard peak. The first peak is at 4.058 minutes, belongs to propanol. The second peak is at 4.188 minutes, belongs to propionaldehyde and the last peak at 4.818 fit it to 1, 3 – propanediol. The other peaks perhaps belong to other chemicals.

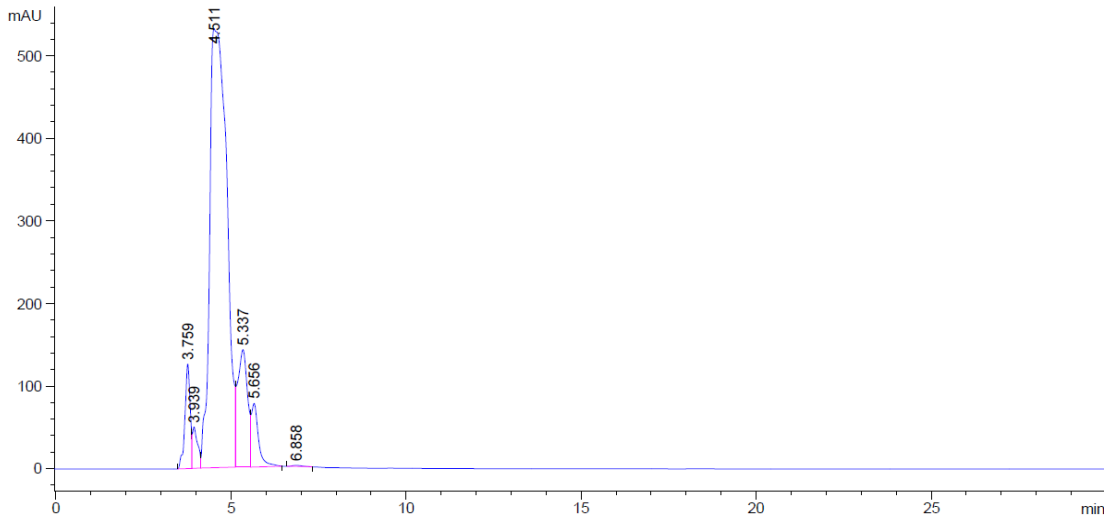


FIGURE 4.13 HPLC Result Used 5.0%Ca, 10%Ni/ ɣ-Al2O3

There are 6 peaks formed in figure above. Only two peaks are known while others are unknown. The known peaks are at 4.511 minutes which is belongs to propylene glycol and at 5.656 belongs to propionaldehyde. The unknown peaks possibly fit in to other chemicals.

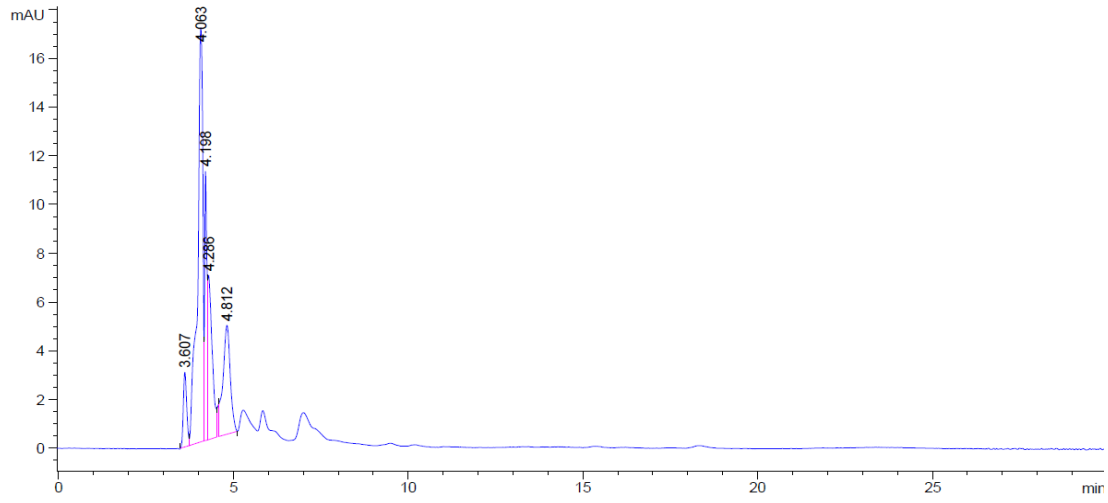


FIGURE 4.14 HPLC Result Used 7.0%Ca, 10%Ni/ ɣ-Al2O3

From the figure above, the highest peak is at 4.063 minutes belongs to propanol. The widest peak at 4.812 minutes belongs to 1, 3 – propanediol. Besides, the peak at 4.286 minutes fit in to ethanol. The peak at 4.198 minutes belongs to glycerol. Lastly, the peak at 3.607 minutes is unidentified peak.

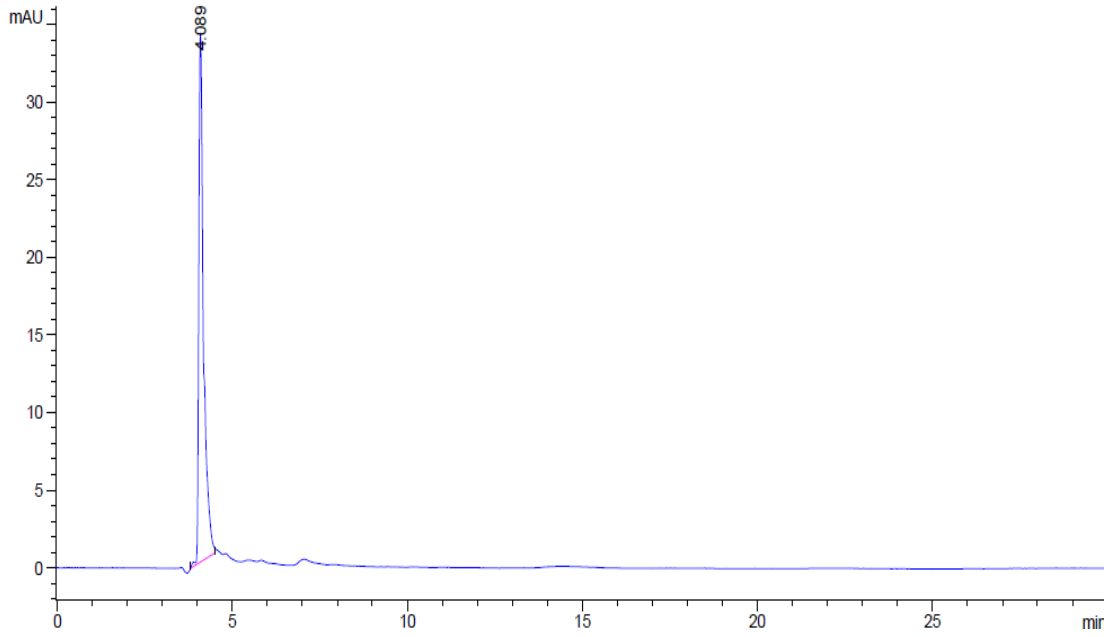


FIGURE 4.15 HPLC Result Used 10%Ca, 10%Ni/ ɣ-Al2O3

From the figure above, only one peak formed which is at 4.089 minutes and belongs to glycerol.

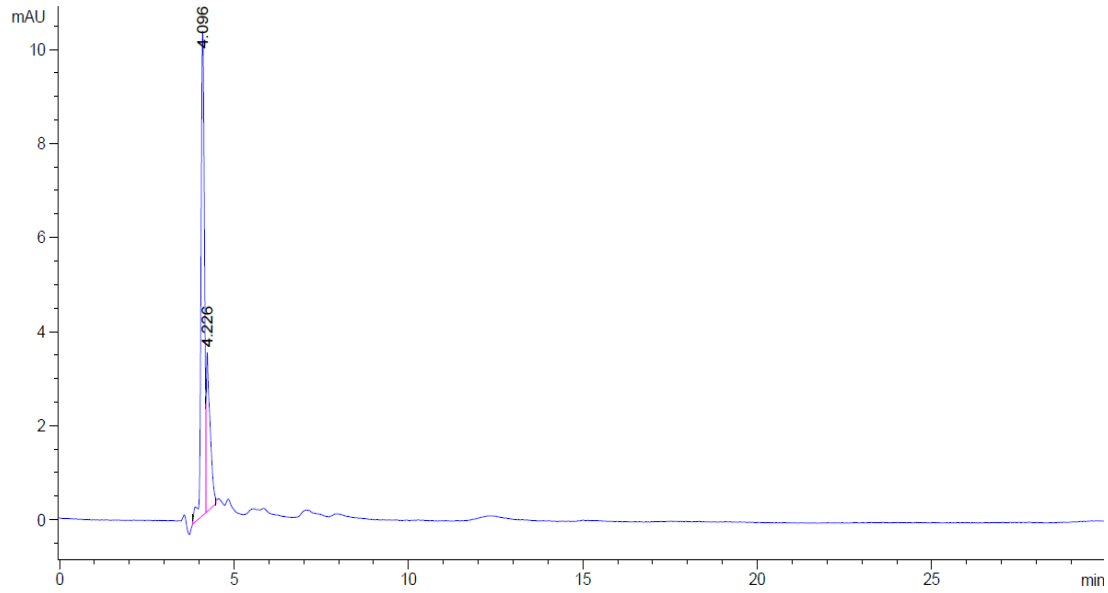


FIGURE 4.16 HPLC Result Used 0.5%Mg, 10%Ni/ ɣ-Al2O3

The highest peak's height is 10.31404 mAU. The retention time is 4.096 minutes. While the second peak' height is 3.38701 mAU with retention time; 4.226 minutes. Both peaks formed belong to glycerol.

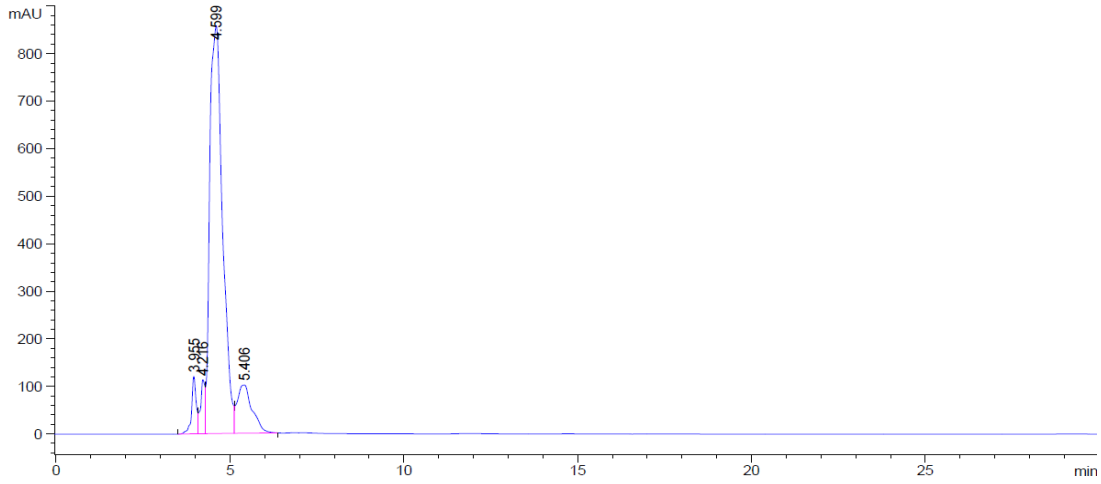


FIGURE 4.17 HPLC Result Used 3.0%Mg, 10%Ni/ ɣ-Al2O3

The highest peak at 4.599 minutes belongs to ethylene glycol while the widest peak is at 5.406 minutes referring to propylene glycol. The peak at 4.216 minutes belongs to glycerol. The last peak at 3.955 minutes belongs to propionaldehyde.

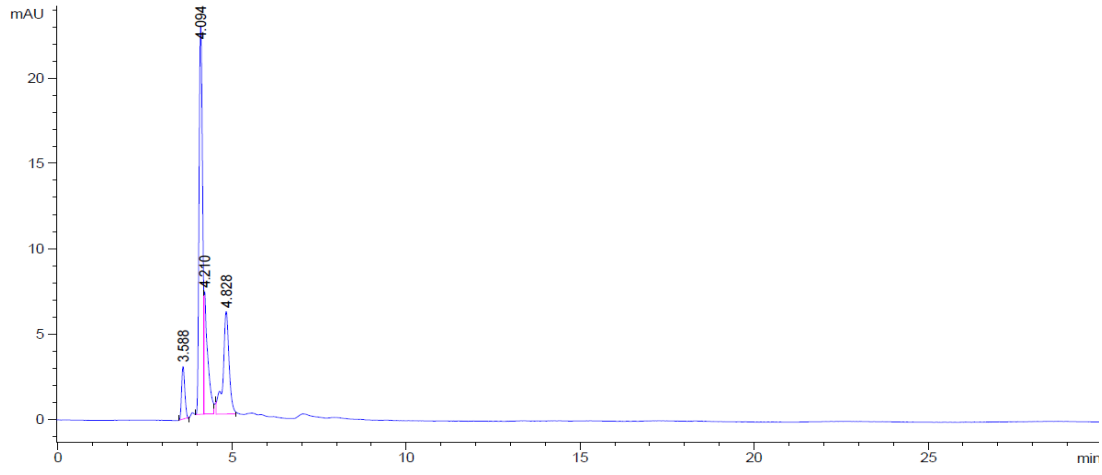


FIGURE 4.18 HPLC Result Used 5.0%Mg, 10%Ni/ ɣ-Al2O3

There are two peaks belong to glycerol which are at 4.094 minutes and 4.210 minutes. There is one peak fit in to propylene glycol at 4.828 minutes. The peak at retention time 3.588 minutes is unknown peak which not appears in the result of standard. May be it's belong to other chemical.

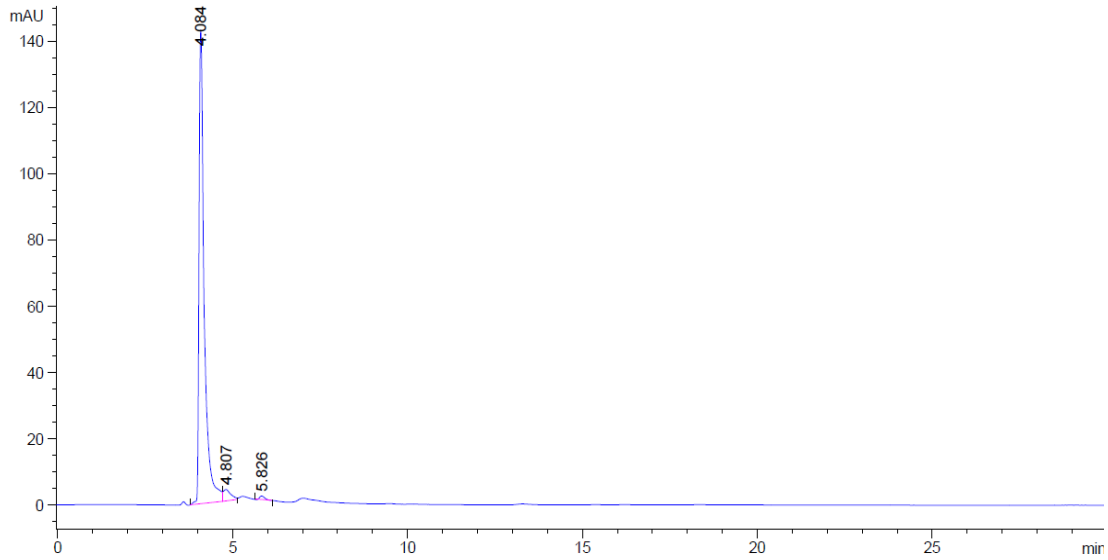


FIGURE 4.19 HPLC Result Used 7.0% Mg, 10%Ni/ ɣ-Al2O3

The highest peak from figure above belongs to glycerol with 4.084 its retention time. The widest peak is at 4.807 fit in to 1, 3 propanediol. The unknown peak formed at 5.826 minutes.

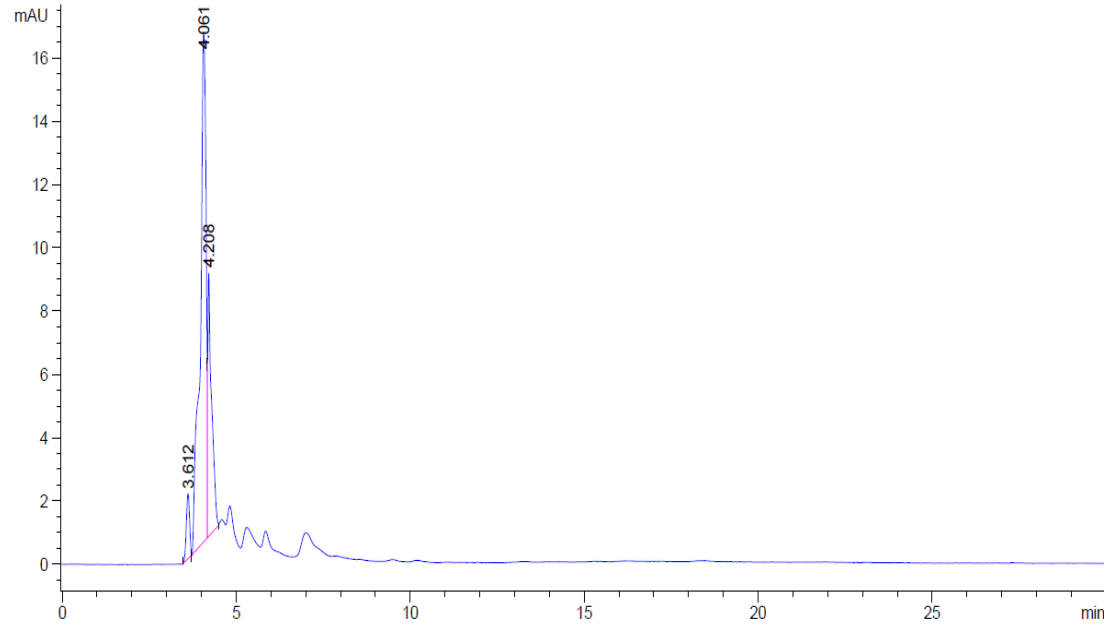


FIGURE 4.20 HPLC Result Used 10%Mg, 10%Ni/ ɣ-Al2O3

From the HPLC result obtained above, the highest and widest peak at 4.061 minutes belongs to propanol. The second highest peak at 4.208 minutes belongs to glycerol. The lowest peak at 3.612 minutes perhaps belongs to other chemical.

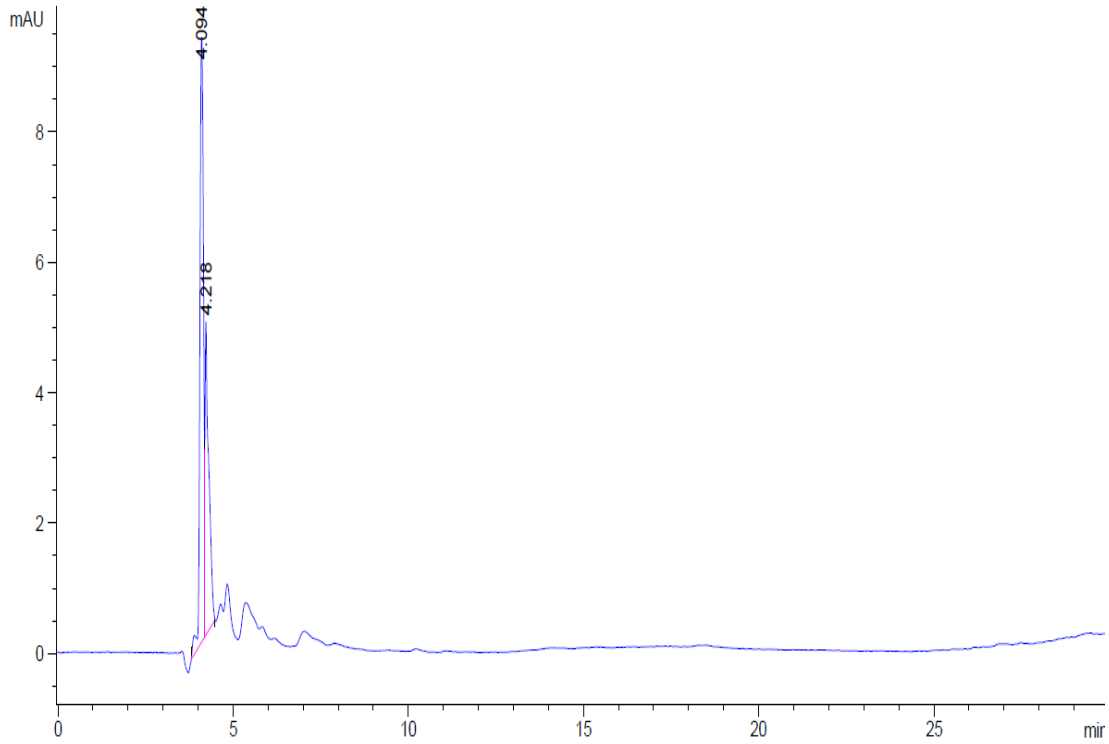


FIGURE 4.21 HPLC Result Used 0.5%Ca + Mg, 10%Ni/ ɣ-Al2O3

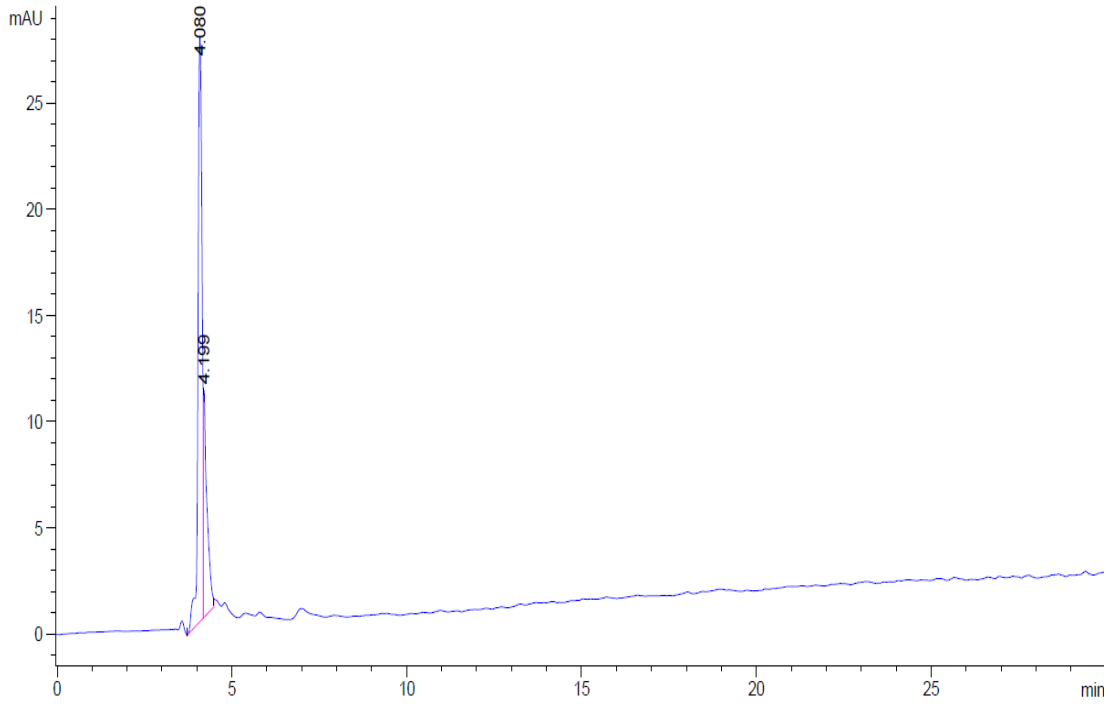


FIGURE 4.22 HPLC Result Used 5.0%Ca + Mg, 10%Ni/ ɣ-Al2O3

There are two peaks appear in the Figure 4.21 and 4.22. The highest peak at Figure 4.21 is 9.29791 mAU and the retention time is 4.094 minutes while the highest peak at Figure 4.22 is 27.60372 mAU and retention time is 4.080 minutes. Whereas the second peak's height at Figure 4.21 is 4.82067 mAU with retention time 4.218 minutes. Last but not least, the second highest peak at Figure 4.22 is 10.73289 mAU with 4.199 minutes its retention time. All of the peaks belong to glycerol.

TABLE 4.5 Conversion of Glycerol

Samples	**Conversion of Glycerol (mol %)**	**Value Added Chemicals Produced**
Glycerol	0.00	-
10% Ni/ɣ-Al_2O_3	71.61	Propionaldehyde, Ethanol
0.5% Ca, 10% Ni/ɣ-Al_2O_3	0.00	-
3% Ca, 10% Ni/ ɣ-Al_2O_3	100	Propanol, Propionaldehyde, 1,3 - propanediol
5% Ca, 10% Ni/ ɣ-Al_2O_3	100	Propionaldehyde, Propylene glycol
7% Ca, 10% Ni/ ɣ-Al_2O_3	86.53	Propanol, Ethanol, 1,3 - propanediol
10% Ca, 10% Ni/ ɣ-Al_2O_3	0.00	-
0.5% Mg, 10% Ni/ɣ-Al_2O_3	0.00	-
3% Mg, 10% Ni/ ɣ-Al_2O_3	96.29	Propionaldehyde, Ethylene glycol, Propylene glycol
5% Mg, 10% Ni/ ɣ-Al_2O_3	30.33	Propylene glycol
7% Mg, 10% Ni/ ɣ-Al_2O_3	4.29	1,3 - propanediol
10% Mg, 10% Ni/ ɣ-Al_2O_3	76.02	Propanol
0.5% Ca + Mg, 10% Ni/ ɣ-Al_2O_3	0.00	-
5% Ca + Mg, 10% Ni/ ɣ-Al_2O_3	0.00	-

In Aqueous Phase Reforming, the presence of catalyst needed just to speed up the reaction by reducing the activation energy. Based on table above, it shows that by using catalysts 3% Ca, 10% Ni/ ɣ-Al_2O_3 and 5% Ca, 10% Ni/ ɣ-Al_2O_3 , it managed to fully convert 1wt% glycerol solution to value added chemicals in 30 minutes which is the reaction time. From the finding of previous study, alkaline and alkaline earth metals (Ca/Mg) are used to increase catalyst basicity and inhibit the formation of coking [49]. Consequently, the presence of modified catalyst will improve the APR reaction of glycerol.

From the results above, the addition of 3% alkaline metals into the support seems to be optimum amount of metals in order to have good APR reaction. This is because the total conversion of glycerol for this amount is higher compare to others which are 100% for calcium metal and 96.29% for magnesium metals. Besides, it also can produce many useful chemicals such as propanol, propionaldehyde, 1, 3 – propanediol, ethylene glycol and propylene glycol

But, there are five sample failed to function as catalyst for APR reaction which are 0.5% Ca, 10% Ni/ɣ-Al_2O_3, 0.5% Mg, 10% Ni/ɣ-Al_2O_3, 10.0% Ca, 10% Ni/ɣ-Al_2O_3, 0.5% Ca + Mg, 10% Ni/ɣ-Al_2O_3 and 5.0% Ca + Mg, 10% Ni/ɣ-Al_2O_3. However, by referring to literature study, supposedly the presence of promoter will enhance the reaction but for this study the result is vice versa which the presence of promoter (0.5% Ca or 0.5% Mg) did not gave impact to the APR reaction. There is possibility carbon deposited at the catalysts that make it deactivate. It same goes to other catalysts which no reaction occurred. There is also possibility carbon deposited at the catalysts that make it deactivate. The other logic possibility that cause catalyst not effectively function is the decreasing of surface area. The surface area of the catalyst decrease, the space for reaction takes place also decrease. This statement is supported with the result from BET analysis. The surface area of catalyst reduced when the composition of element increase. But this reason is not the crucial one.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Based on the researches that had been carried out, all the objectives of this study have been fully achieved. Thirteen samples of different compositions of calcium and magnesium over gamma alumina support have been synthesized using wetness impregnation method.

The synthesized catalysts have been characterized using a few techniques such XRD, BET surface area analysis, SEM, FESEM and TPR. XRD used to discover species present and degree of crystallinity. The addition of calcium and magnesium increased the intensity of the catalyst. From BET analysis, it was found that the addition of metals like nickel, calcium and magnesium decreased the surface area, pore volume and size. SEM and FESEM were used to study the morphology of the catalysts. From the images that have been captured, the particles were well dispersed on the support. The purpose of TPR analysis is to know the degree of reducibility of the catalyst. The reduction temperature of 10% Ni is 660°C.

The main objective of this project is to study the potential value added chemicals can be produce from aqueous phase reforming (APR) of glycerol using Ni/ɣ-Al_2O_3 catalyst promoted or bimetallic couple with Group II metals (Ca/Mg) are achieved. The catalytic activity gamma alumina supported nickel; calcium and magnesium were evaluated in autoclave reactor at 230°C, 10 bar 450 rpm. The results obtained from the reactor were acceptable. The addition of 3% alkaline metals into the support seems to be optimum amount of metals in order to have good APR reaction. The value added chemicals that have been produced that useful to industry are 1, 3-propanediol, propionaldehyde, propylene glycol, propanol, ethanol and ethylene glycol.

5.2 Recommendations

Based on the observations made during this study, a few recommendations that can be drawn for future work in this area are as follows:

1. Vary the operating parameters and glycerol's concentration.

In this study, the operating parameters such as pressure, temperature, etc and concentration of glycerol are fixed. By vary those things, this study become more interesting and much new information can be discovered.

2. Use different catalysts to study the effect of reaction APR of glycerol.

By using different catalyst, possibility to different value of selectivity and percentage of conversion of glycerol is there because different catalyst have different performances rate. Make sure that the prepared catalyst free from carbon in order to have efficient APR reaction.

3. Use GC-MS instead of HPLC

It is recommended to use GC-MS instead of HPLC to analyse the liquid products because GC-MS's result easier to interpret and the outcome is more accurate compare to HPLC.

REFERENCES

[1] U.S Energy Information Administration, "Monthly Biodiesel Production Report," *PETROLEUM & OTHER LIQUIDS*, 2015. [Online]. Available: http://www.eia.gov/biofuels/biodiesel/production/.

[2] Z. Wen, "New Uses for Crude Glycerin from Biodiesel Production," *Introduction*, 2012. [Online]. Available: http://www.extension.org/pages/29264/new-uses-for-crude-glycerin-from-biodiesel-production#.VPVwf3yUfIN.

[3] Union of Concerned Scientists, "Benefits of Renewable Energy Use." [Online]. Available: http://www.ucsusa.org/clean_energy/our-energy-choices/renewable-energy/public-benefits-of-renewable.html#.VRquSvyUfIM.

[4] National Renewable Energy Laboratory, "From Biomass to Biofuels," *U.S Department Energy*, 2006.

[5] European Commission, "Economic analysis of EU agriculture," Brussels, 2007.

[6] Y.-C. Lin, "Catalytic valorization of glycerol to hydrogen and syngas," *Int. J. Hydrogen Energy*, vol. 38, no. 6, pp. 2678–2700, 2013.

[7] National Institute of Health, "Gycerol," *Compound Summary for CID 753*. [Online]. Available: http://pubchem.ncbi.nlm.nih.gov/compound/glycerol#section=Information-Sources.

[8] W. De Greyt, "Introduction on Glycerol as co-product from biodiesel plants," 2011, p. 12.

[9] P&G Chemicals, "GLYCERIN," 2015. [Online]. Available: http://www.pgchemicals.com/products/glycerin/.

[10] M. Melissa, "GLYCEROL," 2010. [Online]. Available: https://myorganicchemistry.wikispaces.com/Glycerol. .

[11] Transparency Market Research, "Report: glycerol market expected to reach $2.1 billion in 2018," *BIODIESEL MAGAZINE*, BBI International, 2013.

[12] T. Valliyappan, N. N. Bakhshi, and A. K. Dalai, “Pyrolysis of glycerol for the production of hydrogen or syn gas,” *Bioresour. Technol.*, vol. 99, no. 10, pp. 4476–4483, 2008.

[13] F. Pompeo, G. Santori, and N. N. Nichio, “Hydrogen and/or syngas from steam reforming of glycerol. Study of platinum catalysts,” *Int. J. Hydrogen Energy*, vol. 35, no. 17, pp. 8912–8920, 2010.

[14] D. C. Rennard, J. S. Kruger, and L. D. Schmidt, “Autothermal Catalytic Partial Oxidation of Glycerol to Syngas and to Non-Equilibrium Products,” *ChemSusChem*, vol. 2, no. 1, pp. 89–98, 2009.

[15] K. Kenyon, “Renewable Hydrogen Demonstration and Education Project.” Madison, WI, 2003.

[16] A. Kirilin, “Aqueous-phase reforming of renewables for selective hydrogen production in the presence of supported platinum catalysts,” 2013.

[17] BTG, “Liquid phase processing.” BTG Biomass Technology Group & BlueBear, 2012.

[18] G. Wen, Y. Xu, H. Ma, Z. Xu, and Z. Tian, “Production of hydrogen by aqueous-phase reforming of glycerol,” *Int. J. Hydrogen Energy*, vol. 33, pp. 6657–6666, 2008.

[19] Y. Guo, X. Liu, M. U. Azmat, W. Xu, J. Ren, Y. Wang, and G. Lu, “Hydrogen production by aqueous-phase reforming of glycerol over Ni-B catalysts,” *Int. J. Hydrogen Energy*, vol. 37, no. 1, pp. 227–234, 2012.

[20] Z. Tang, J. Monroe, J. Dong, T. Nenoff, and D. Weinkauf, “Platinum-Loaded NaY Zeolite for Aqueous-Phase Reforming of Methanol and Ethanol to Hydrogen,” *Ind. Eng. Chem. Res.*, vol. 48, no. 5, pp. 2728–2733, 2009.

[21] G. Wen, Y. Xu, Z. Xu, and Z. Tian, “Characterization and Catalytic Properties of the Ni/Al2O3 Catalysts for Aqueous-phase Reforming of Glucose,” *Catal. Letters*, vol. 129, no. 1–2, pp. 250–257, 2009.

[22] A. Iriondo, V. L. Barrio, J. F. Cambra, P. L. Arias, M. B. Güemez, R. M. Navarro, M. C. Sánchez-Sánchez, and J. L. G. Fierro, “Hydrogen Production from Glycerol Over Nickel Catalysts Supported on Al2O3 Modified by Mg, Zr, Ce or La,” *Top. Catal.*, vol. 49, no. 1–2, pp. 46–58, 2008.

[23] Z. Yaakob, M. R. Yosfiah, L. J. Minggu, M. A. Ibrahim, and W. R. W. Daud, “Effects of Ni and Pd metals catalyst on Gamma Alumina support,” in *Proceedings of the 1st International Conference on Natural Resources Engineering & Technology*, 2006.

[24] R. L. Manfro, A. F. da Costa, N. F. P. Ribeiro, and M. M. V. M. Souza, “Hydrogen production by aqueous-phase reforming of glycerol over nickel

catalysts supported on CeO2," *Fuel Process. Technol.*, vol. 92, no. 3, pp. 330–335, 2011.

[25] N. Luo, X. Fu, F. Cao, T. Xiao, and P. P. Edwards, "Glycerol aqueous phase reforming for hydrogen generation over Pt catalyst – Effect of catalyst composition and reaction conditions," *Fuel*, vol. 87, no. 17–18, pp. 3483–3489, 2008.

[26] R. D. Cortright, R. R. Davda, and J. A. Dumesic, "Hydrogen from catalytic reforming of biomass-derived hydrocarbons in liquid water," *Nature*, vol. 418, no. 6901, pp. 964–967, 2002.

[27] A. O. Menezes, M. T. Rodrigues, A. Zimmaro, L. E. P. Borges, and M. A. Fraga, "Production of renewable hydrogen from aqueous-phase reforming of glycerol over Pt catalysts supported on different oxides," *Renew. Energy*, vol. 36, no. 2, pp. 595–599, 2011.

[28] K. D. Pathak, "Catalytic Conversion of Glycerol to Value-Added Liquid Chemicals ," pp. 1–166, 2005.

[29] P. V.Tuza, R. L.Manfro, N. F. P. Ribeiro, and M. M. V. M. Souza, "Production of renewable hydrogen by aqueous-phase reforming of glycerol over Ni–Cu catalysts derived from hydrotalcite precursors," *Renew. Energy*, vol. 50, no. 0, pp. 408–414, 2013.

[30] D. L. King, L. Zhang, G. Xia, A. M. Karim, D. J. Heldebrant, X. Wang, T. Peterson, and Y. Wang, "Aqueous phase reforming of glycerol for hydrogen production over Pt–Re supported on carbon," *Appl. Catal. B Environ.*, vol. 99, no. 1–2, pp. 206–213, 2010.

[31] K. W. Siew, H. C. Lee, J. Gimbun, and C. K. Cheng, "Characterization of La-promoted Ni/Al2O3 catalysts for hydrogen production from glycerol dry reforming," *J. Energy Chem.*, vol. 23, no. 1, pp. 15–21, 2014.

[32] Z. Cheng, Q. Wu, J. Li, and Q. Zhu, "Effects of promoters and preparation procedures on reforming of methane with carbon dioxide over Ni/Al 2 O 3 catalyst," *Catal. Today*, vol. 30, no. 1, pp. 147–155, 1996.

[33] C.-H. Zhou, J. N. Beltramini, Y.-X. Fan, and G. Q. Lu, "Chemoselective catalytic conversion of glycerol as a biorenewable source to valuable commodity chemicals," *Chem. Soc. Rev.*, vol. 37, no. 3, pp. 527–549, 2008.

[34] S. Ayalur Chattanathan, "Hydrogen Production from Renewable Bio-Based Sources," pp. 1–125, 2014.

[35] H. Chu, "The Preparation of Catalytic Materials," National Cheng Kung University.

[36] Direct Industry, “Catalyzer test station TPDRO 1100.” [Online]. Available: http://www.directindustry.com/prod/thermo-scientific-scientific-instruments-aut/product-7217-1042317.html.

[37] Australian Microscopy and Microanalysis Research Facility, “Background Information,” 2014. [Online]. Available: http://www.ammrf.org.au/myscope/xrd/background/.

[38] Gold App Instruments Corporation China, “HIGH PRESSURE GAS SORPTION,” 2015. [Online]. Available: http://www.exportersindia.com/gold-app-instruments/products.htm.

[39] Lucideon, “Brunauer-Emmett-Teller (BET) Surface Area Analysis and Barrett-Joyner-Halenda (BJH) Pore Size and Volume Analysis,” 2015. [Online]. Available: http://www.ceram.com/testing-analysis/techniques/brunauer-emmett-teller-surface-area-analysis-barrett-joyner-halenda-pore-size-and-volume-analysis/.

[40] Nanotechnology Now, “JEOL Introduces New Versatile FE-SEM Series for Sub-Nanometer Imaging and Analysis of Nanostructures and Magnetic Samples,” 2015. [Online]. Available: http://www.nanotech-now.com/news.cgi?story_id=44946.

[41] Instituto Superior Tecnico, “Other Equipments,” *CQE*, 2014. [Online]. Available: http://groups.ist.utl.pt/~cqe.daemon/members-contacts/scientific-topics/other-equipments/.

[42] premex reactor ag, “P-Linie.” [Online]. Available: http://www.premex-reactorag.ch/index.php?page=452.

[43] Ali Ebshish, Zahira Yaakob, Binitha Narayanan, Ahmad Bshish, and W. R. W. Daud, “The Activity of Ni-Based Catalysts on Steam Reforming of Glycerol for Hydrogen Production,” *Int. J. Integr. Eng.*, vol. 3, no. 1, pp. 5–8, 2011.

[44] G. Wu, S. Li, C. Zhang, T. Wang, and J. Gong, “Glycerol steam reforming over perovskite-derived nickel-based catalysts,” *Appl. Catal. B Environ.*, vol. 144, no. 0, pp. 277–285, 2014.

[45] I. W. Chen, S. Y. Lin, and D. Shiue, *Calcination of Nickel/Alumina Catalyst*. Ind. Eng. Chem. Res, 1988.

[46] R. M. de Almeida, H. V. Fjardo, D. Z. Mezalira, G. B. Nuernberg, L. K. Noda, L. F. D. Probst, and N. L. V. Carreno, “Preparation and evaluation of porous nickel-alumina spheres as catalyst in the production of hydrogen from decomposition of methane,” *J. Mol. Catal.*, no. 259, pp. 328–335, 2006.

[47] S. Lowell, J. E. Shields, M. A. Thomas, and M. Thommes, *Characterization of Porous Solids and Powders: Surface Area, Pore Size and Density*. AH Dordrecht, The Netherlands: Kluwer Academic Publishers, 2004.

[48] C. Li and Y. W. Chen, “Temperature-programmed-reduction studies of nickel oxide/alumina catalysts: effects of the preparation method,” *Thermochim. Acta*, no. 256, pp. 457–465, 1995.

[49] G. Yang, H. Yu, X. Huang, F. Peng, and H. Wang, “Effect of calcium dopant on catalysis of Ir/La2O3 for hydrogen production by oxidative steam reforming of glycerol,” *Appl. Catal. B Environ.*, vol. 127, no. 0, pp. 89–98, 2012.

APPENDICES

Appendix I: Calculation for Catalysts

Amount of support and metal for catalyst preparation

Sample size: 25 gram catalyst

Mass of catalyst = mass of metal + mass of support

Percentage (%) of metal loading: 10 wt% metal of catalyst

Amount of Nickel Nitrate Hexahydrate, Calcium Chloride Dehydrate and Magnesium Nitrate Hexahydrate

TABLE I.1 Composition of Catalysts

Sample	Composition of Al_2O_3:Ni:Ca:Mg	Sample	Composition of Al_2O_3:Ni:Ca:Mg
10% Ni/ɣ-Al_2O_3	90:10:0:0	3% Mg, 10% Ni/ ɣ-Al_2O_3	87:10:0:3
0.5% Ca, 10% Ni/ɣ-Al_2O_3	89.5:10:0.5:0	5% Mg, 10% Ni/ ɣ-Al_2O_3	85:10:0:5
3% Ca, 10% Ni/ ɣ-Al_2O_3	87:10:3:0	7% Mg, 10% Ni/ ɣ-Al_2O_3	83:10:0:7
5% Ca, 10% Ni/ ɣ-Al_2O_3	85:10:5:0	10% Mg, 10% Ni/ ɣ-Al_2O_3	80:10:0:10
7% Ca, 10% Ni/ ɣ-Al_2O_3	83:10:7:0	0.5% Ca + Mg, 10% Ni/ ɣ-Al_2O_3	89:10:0.5:0.5
10% Ca, 10% Ni/ ɣ-Al_2O_3	80:10:10:0	5.0% Ca + Mg, 10% Ni/ɣ-Al_2O_3	80:10:5:5
0.5% Mg, 10% Ni/ɣ-Al_2O_3	89.5:10:0:0.5		

Table I.1 shows the different compositions of Nickel, Calcium and Magnesium used for catalyst preparation.

Molecular weight of Nickel Nitrate Hexahydrate: 290.81 g/mol

Molecular weight of Calcium Chloride Dehydrate: 147.02 g/mol

Molecular weight of Magnesium Nitrate Hexahydrate : 256.41 g/mol

Atomic mass Nickel: 58.7 g/mol

Atomic mass Calcium: 40.1 g/mol

Atomic mass Magnesium: 24.3 g/mol

General formula used:

Mass of metal loading = $\frac{Percentage\ (\%) of\ metal\ loading}{100\ \%} \times mass\ of\ catalyst$

Mass of salt needed = $\frac{Molecular\ mass\ of\ salt}{Atomic\ mass\ of\ metal} \times mass\ of\ metal\ loading$

Example:

Mass of Nickel loading = $\frac{10}{100} \times 25\ g\ of\ catalyst$ = 2.5 g of Nickel

Mass of Nickel Nitrate Hexahydrate needed

= $\frac{290.81 \frac{g}{mol}\ \mathrm{Ni(NO3)2.6H2O}}{58.7 \frac{g}{mol}\ Ni} \times 2.5\ g\ Ni$ = 12.39 g $Ni(NO_3)_2.6H_2O$

TABLE I.2 Calculated Mass of Metals in Catalysts

Sample	**ɣ - Al_2O_3 needed (g)**	**$Ni(NO_3)_2.6H_2O$ needed (g)**	**$CaCl_2.2H2O$ needed (g)**	**$Mg(NO_3)_2.6H2O$ needed (g)**
10% Ni/ɣ-Al_2O_3	22.5	12.39	-	-
0.5% Ca, 10% Ni/ɣ-Al_2O_3	22.38	12.39	0.46	
3% Ca, 10% Ni/ ɣ-Al_2O_3	21.75	12.39	2.75	-
5% Ca, 10% Ni/ ɣ-Al_2O_3	21.25	12.39	4.58	-
7% Ca, 10% Ni/ ɣ-Al_2O_3	20.75	12.39	6.42	-
10% Ca, 10% Ni/ ɣ-Al_2O_3	20.00	12.39	9.17	-
0.5% Mg, 10% Ni/ɣ-Al_2O_3	22.38	12.39	-	1.32
3% Mg, 10% Ni/ ɣ-Al_2O_3	21.75	12.39	-	7.91
5% Mg, 10% Ni/ ɣ-Al_2O_3	21.25	12.39	-	13.19
7% Mg, 10% Ni/ ɣ-Al_2O_3	20.75	12.39	-	18.47
10% Mg, 10% Ni/ ɣ-Al_2O_3	20.00	12.39	-	26.38
0.5% Ca + Mg, 10% Ni/ ɣ-Al_2O_3	22.25	12.39	0.46	1.32
5% Ca + Mg, 10% Ni/ ɣ-Al_2O_3	20	12.39	4.58	13.19

Appendix II: Isotherm Linear Plot

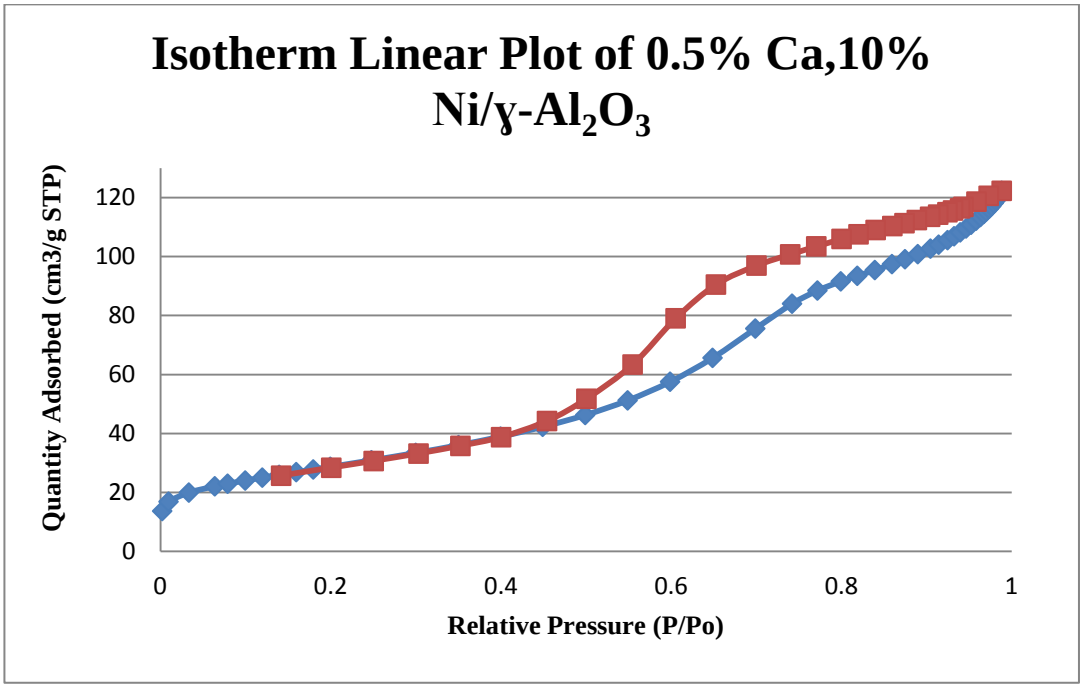


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FIGURE II.1 Isotherm Linear Plot of 0.5% Ca, 10%Ni/ ɣ-Al_2O_3

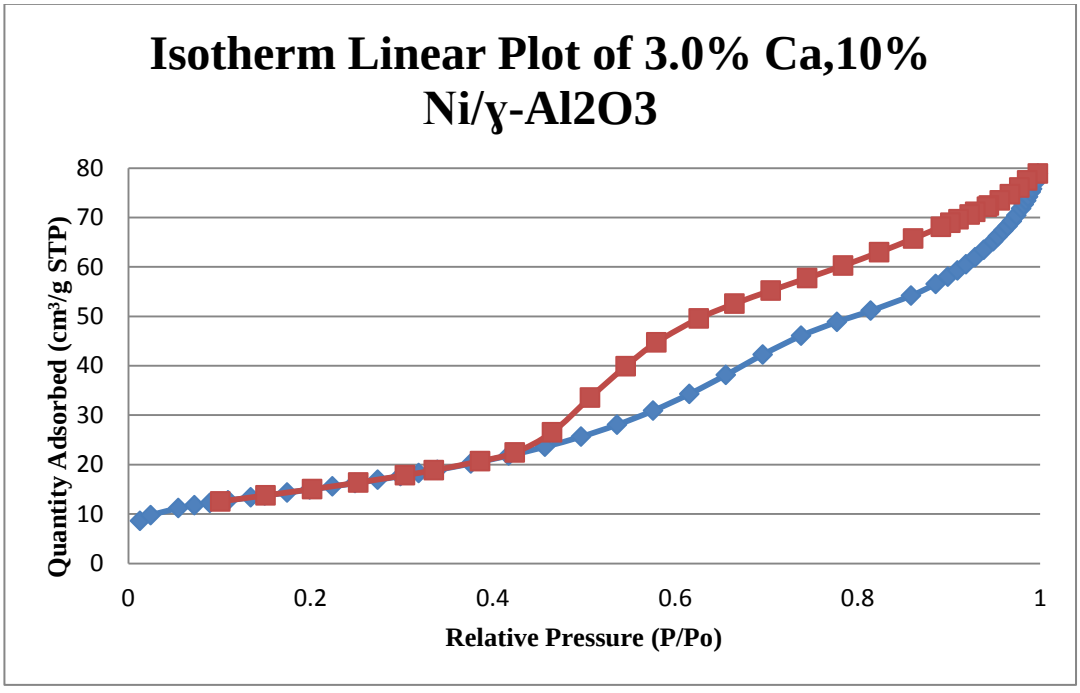

FIGURE II.2 Isotherm Linear Plot of 3.0% Ca, 10%Ni/ ɣ-Al_2O_3

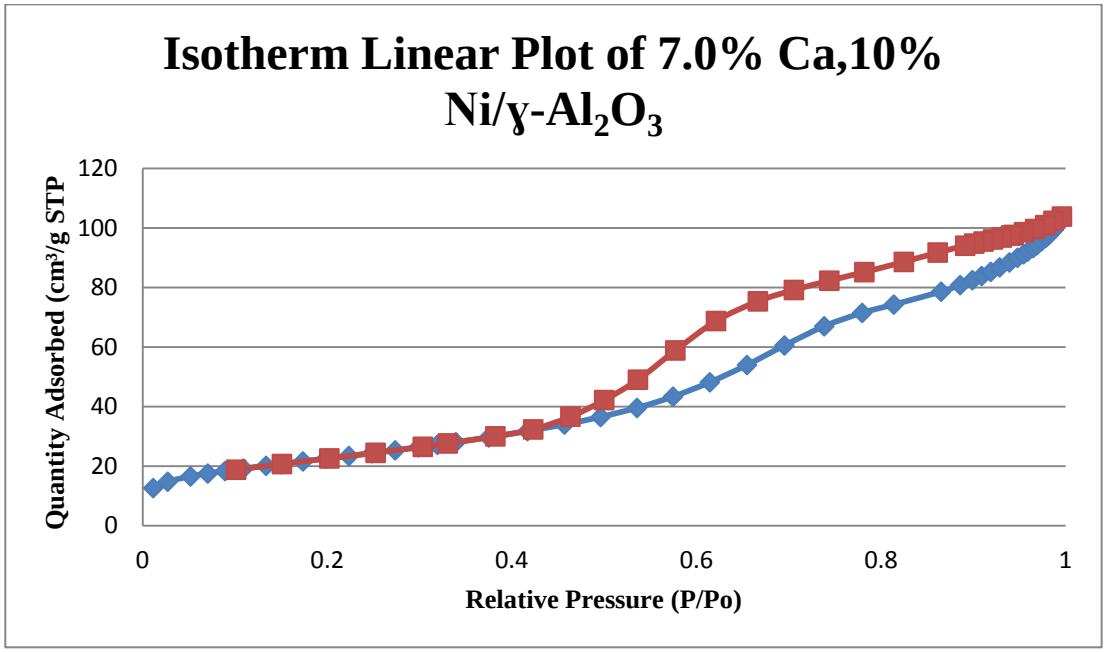

FIGURE II.3 Isotherm Linear Plot of 7.0% Ca, 10%Ni/ ɣ-Al_2O_3

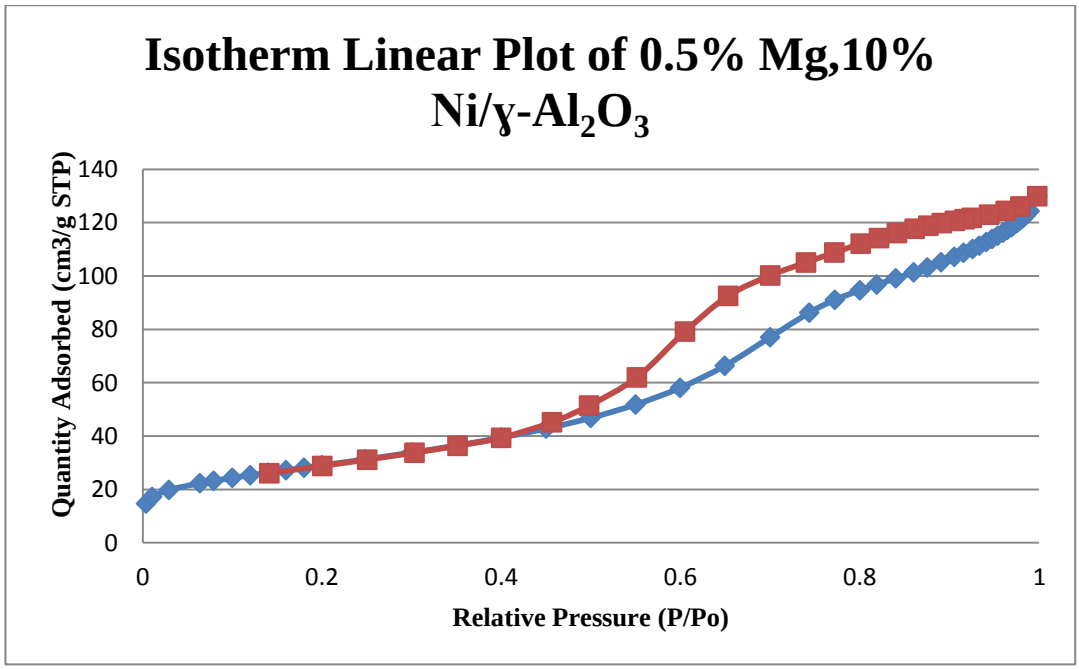

FIGURE II.4 Isotherm Linear Plot of 0.5% Mg, 10%Ni/ ɣ-Al_2O_3

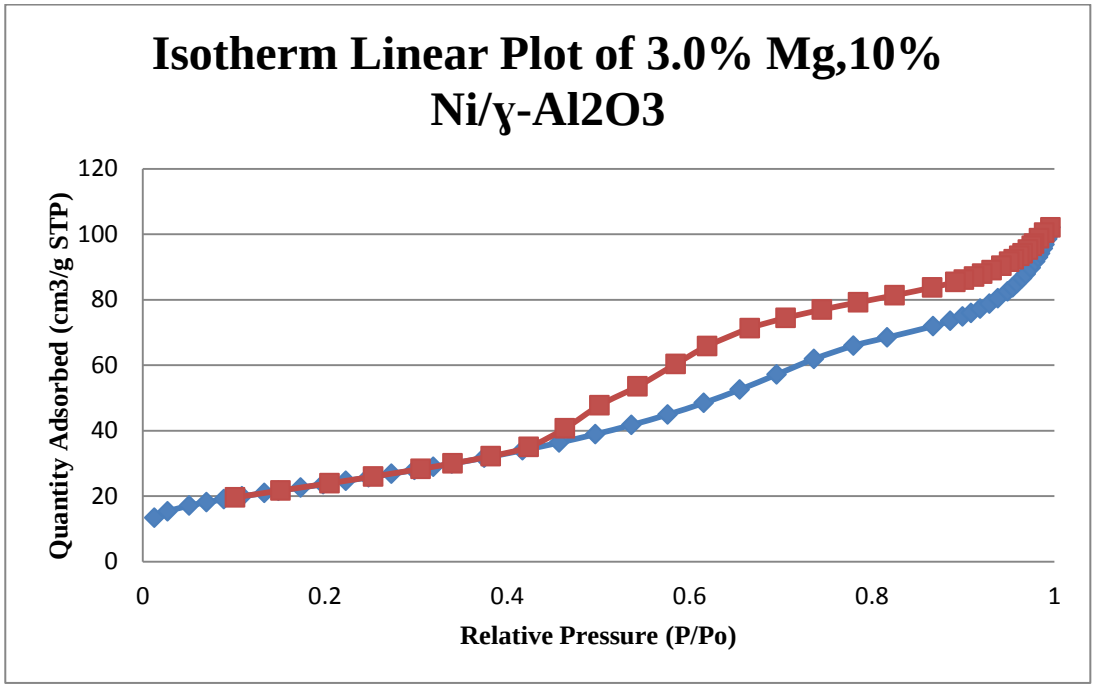

FIGURE II.5 Isotherm Linear Plot of 3.0% Mg, 10%Ni/ ɣ-Al_2O_3

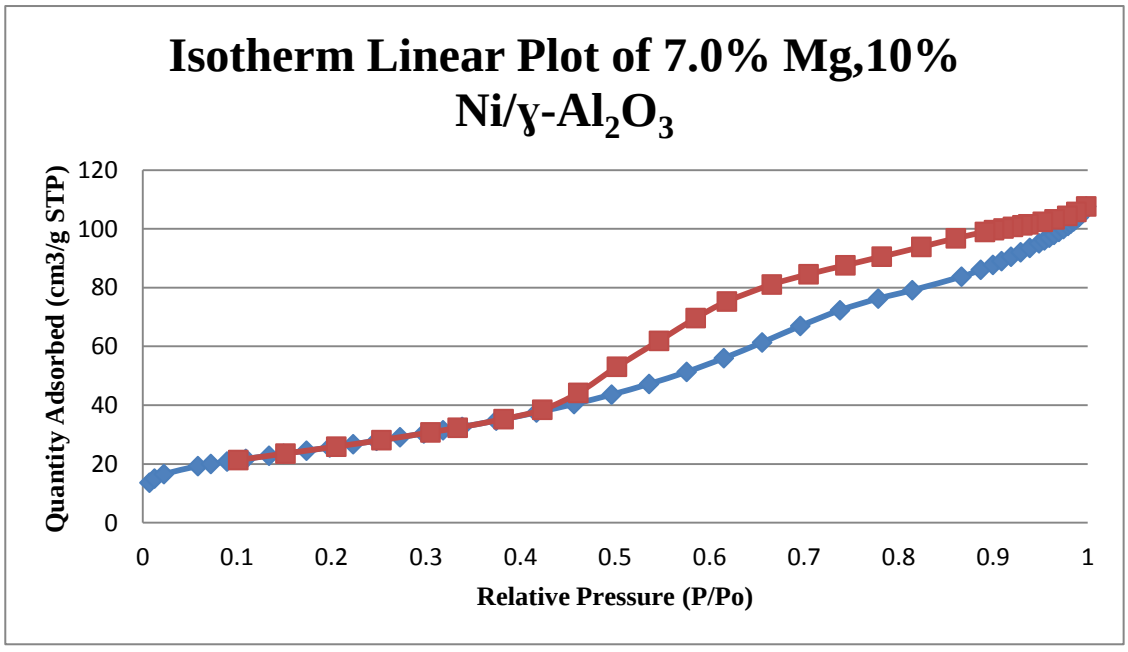

FIGURE II.6 Isotherm Linear Plot of 7.0% Mg, 10%Ni/ ɣ-Al_2O_3

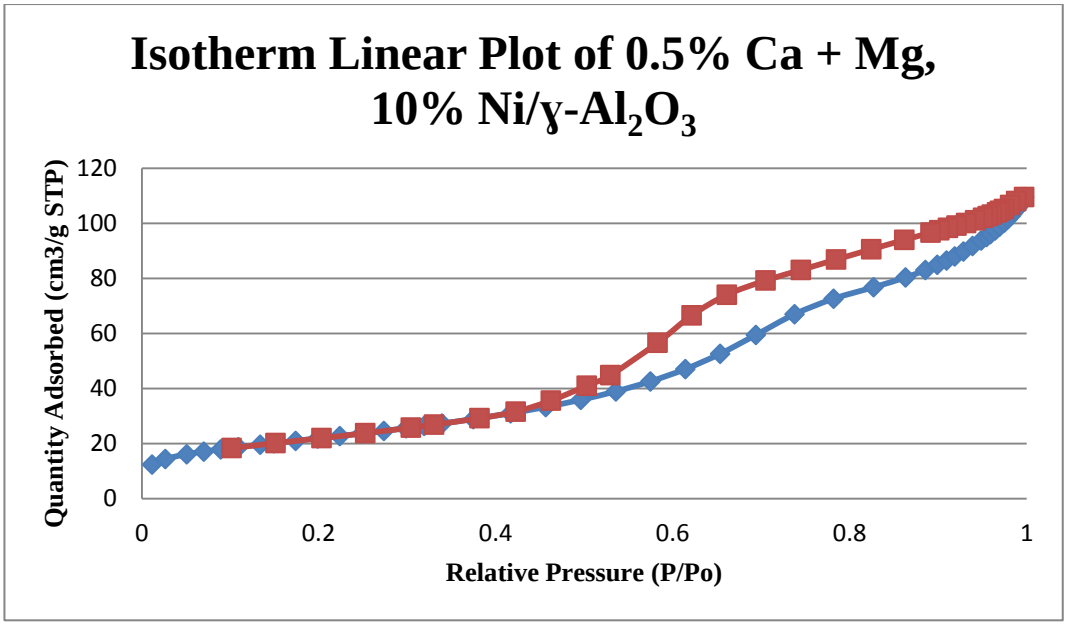

FIGURE II.7 Isotherm Linear Plot of 0.5% Ca + Mg, 10%Ni/ ɣ-Al_2O_3

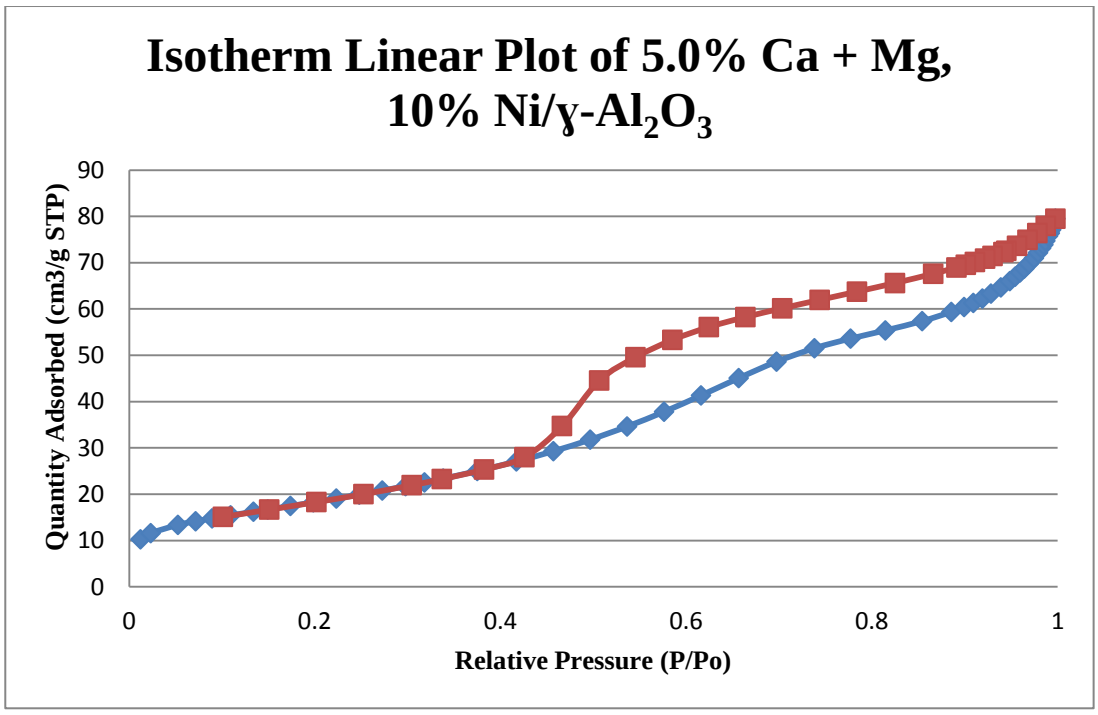

FIGURE II.8 Isotherm Linear Plot of 5.0% Ca + Mg, 10%Ni/ ɣ-Al_2O_3

Appendix III: Raw Data for BET Analysis

TABLE III.1 Isotherm Linear Plot Data for ɣ-Al2O3

Relative Pressure (P/Po)	Quantity Adsorbed (cm^3/g STP)
0.001113	15.4323
0.010167	21.70873
0.032347	25.47799
0.06109	28.17061
0.077943	29.44444
0.099578	30.93829
0.119528	32.22023
0.139461	33.46015
0.159407	34.67145
0.179384	35.87119
0.199357	37.06942
0.246552	39.93842
0.299309	43.31408
0.350031	46.83091
0.39937	50.66276
0.449409	55.10458
0.49898	60.34917
0.54888	66.80254
0.598986	75.09903
0.64943	85.78567
0.701269	98.6309
0.745468	108.4849
0.771191	112.7796
0.799652	116.4659
0.819325	118.6509
0.840258	120.8514
0.860264	123.0867

Appendix IV: HPLC Results for Standard

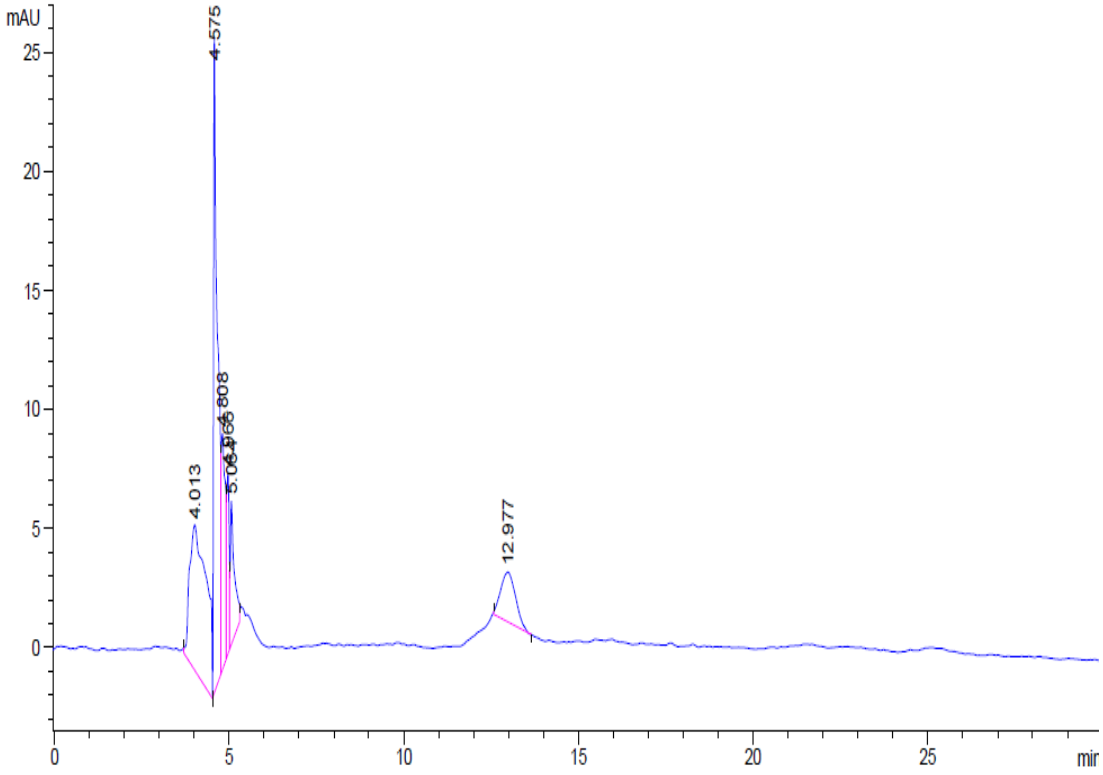

FIGURE IV.1 HPLC Result for 1, 3 – propanediol

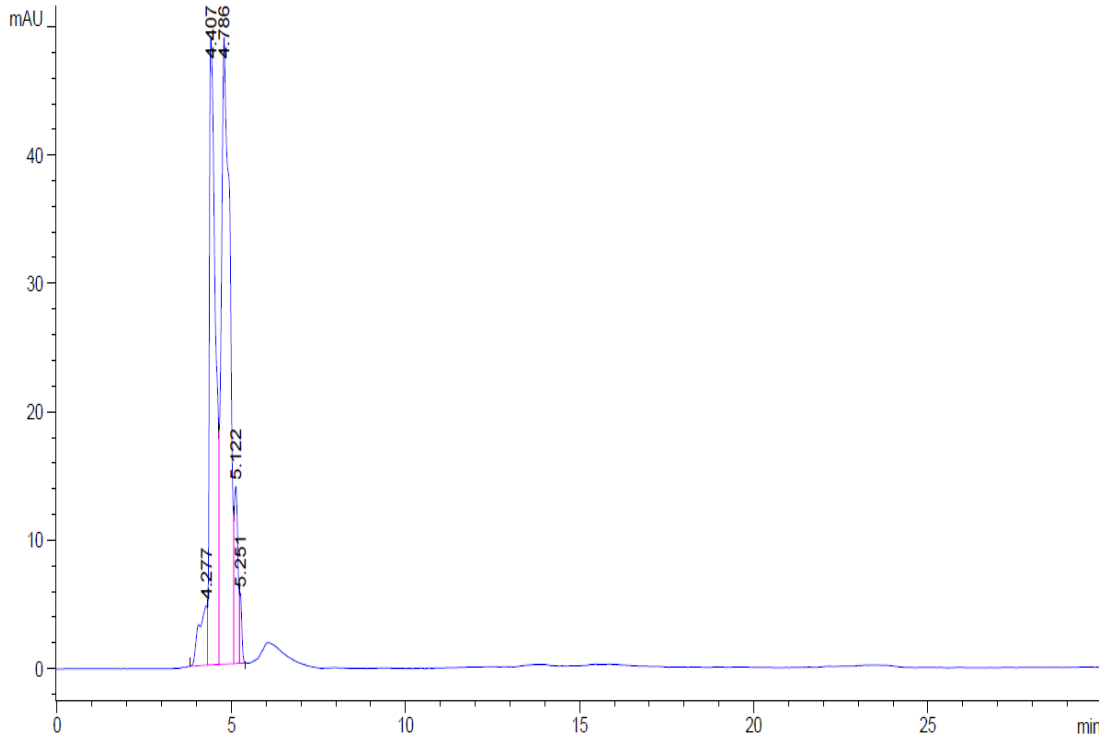

FIGURE IV.2 HPLC Result for Ethanol

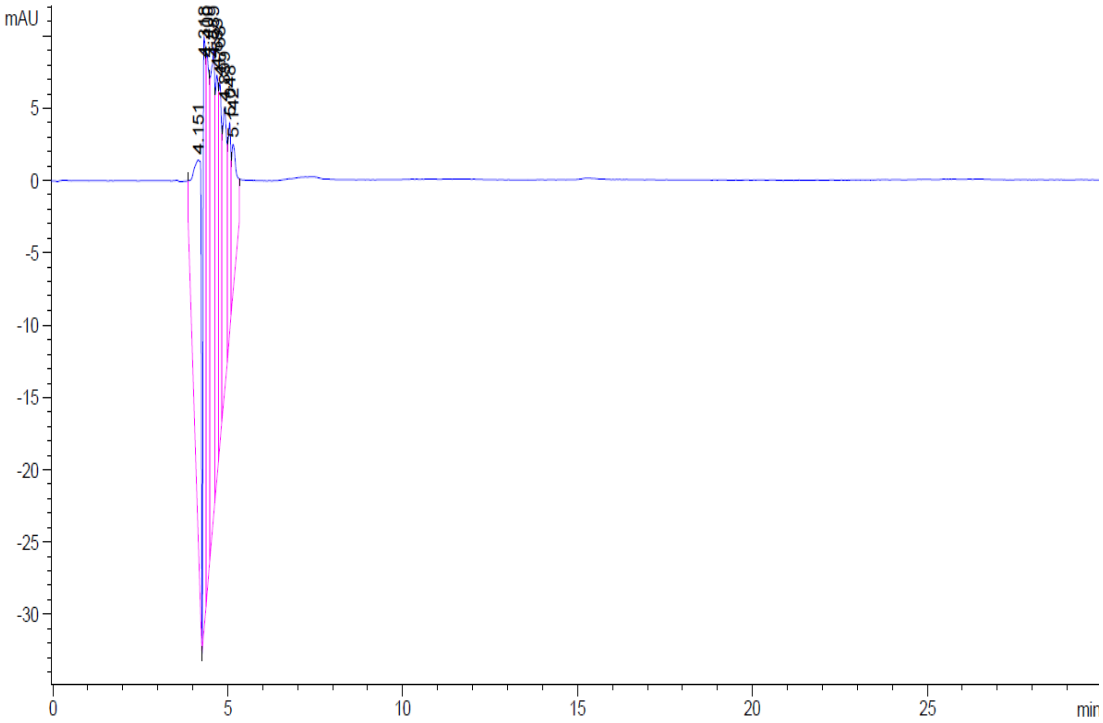

FIGURE IV.3 HPLC Result for Ethylene Glycol

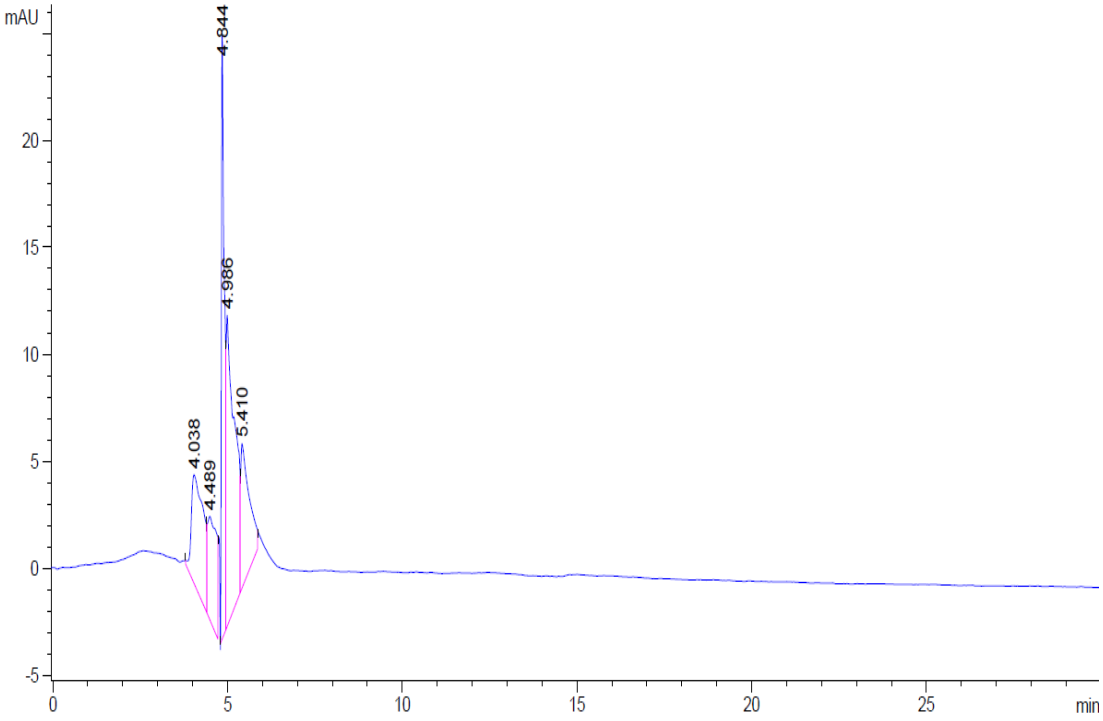

FIGURE IV.4 HPLC Result for Propanol

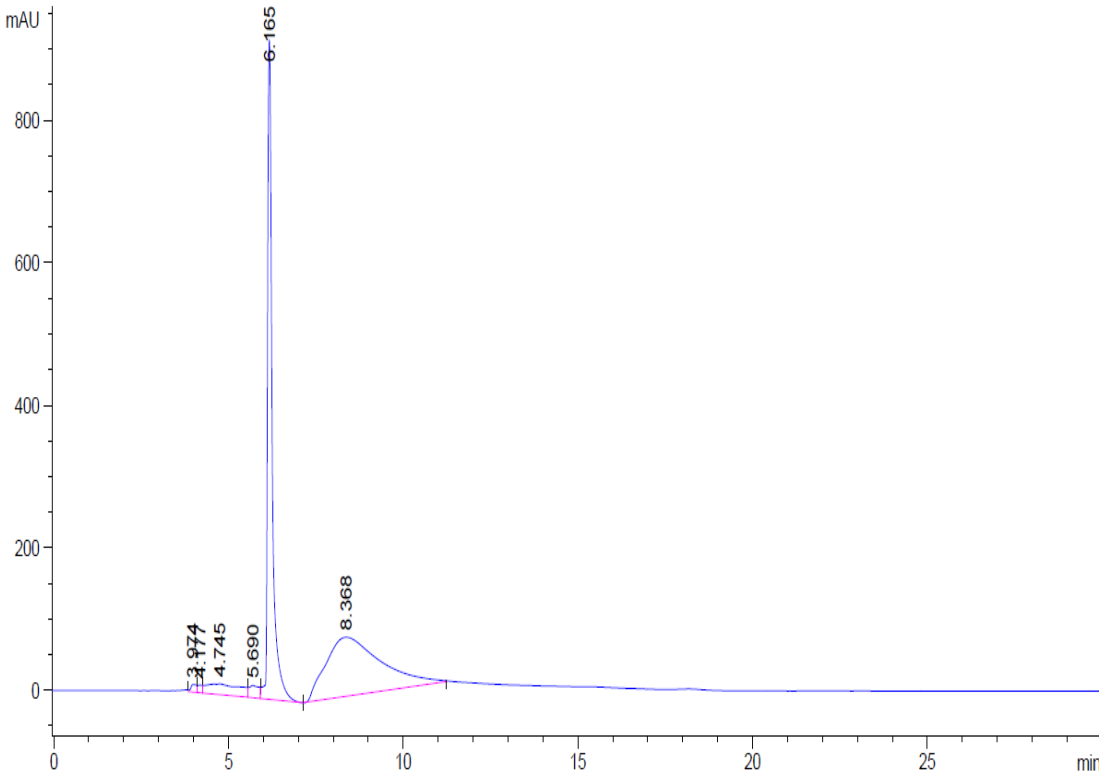

FIGURE IV.5 HPLC Result for Propionaldehyde

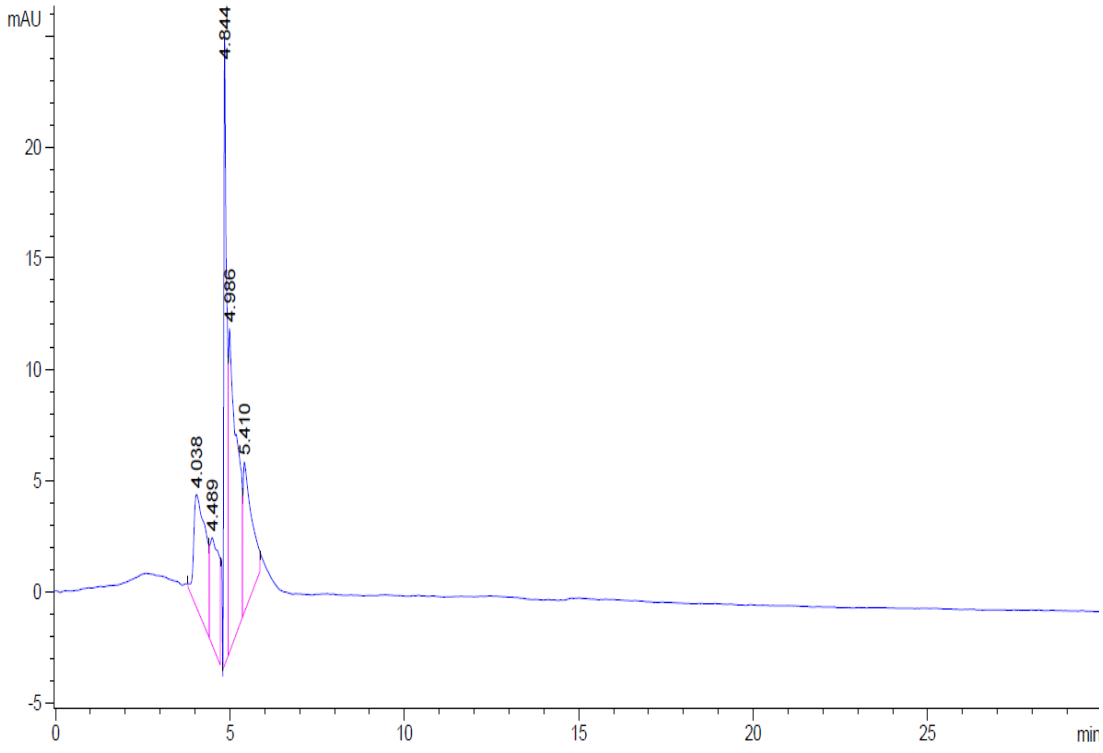

FIGURE IV.6 HPLC Result for Propylene Glycol

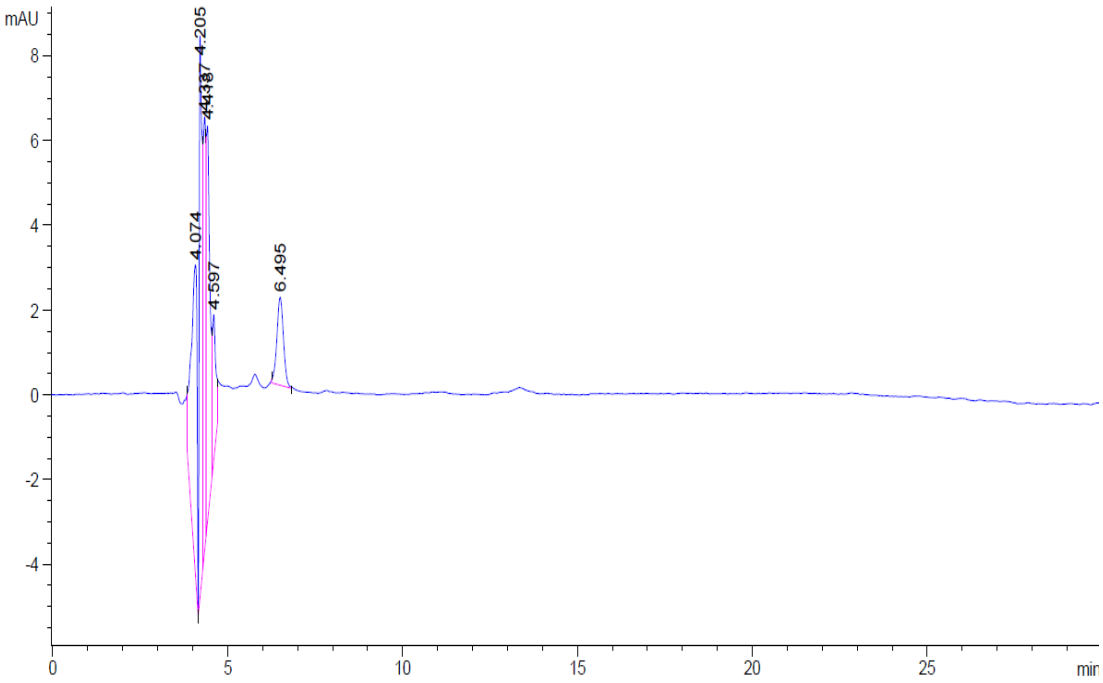

FIGURE IV.7 HPLC Result for Glycerol

Appendix V: Calculation for Conversion of Glycerol

Formula use to calculate the conversion of glycerol:

Peak area = height x width x 0.5

Total area = Peak area 1 + Peak area 2 + …….

Mole % for Peak area 1 = (Peak area 1 / Total area) x 100 %